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(54) **DIATOMACEOUS ENERGY STORAGE DEVICES**

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See application file for complete search history.

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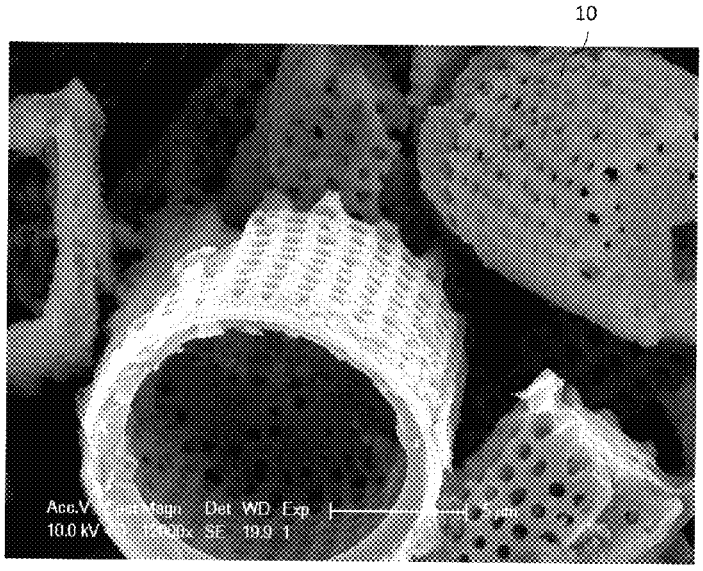
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(57) **ABSTRACT**

The disclosed technology generally relates to energy storage devices, and more particularly to energy storage devices comprising frustules. According to an aspect, a supercapacitor comprises a pair of electrodes and an electrolyte, wherein at least one of the electrodes comprises a plurality of frustules having formed thereon a surface active material. The surface active material can include nanostructures. The surface active material can include one or more of a zinc oxide, a manganese oxide and a carbon nanotube.

20 Claims, 46 Drawing Sheets



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continuation-in-part of application No. 15/808,757, filed on Nov. 9, 2017, now Pat. No. 10,109,864, which is a continuation of application No. 15/406,407, filed on Jan. 13, 2017, now Pat. No. 9,825,305, which is a continuation of application No. 14/745,709, filed on Jun. 22, 2015, now Pat. No. 9,548,511, which is a continuation-in-part of application No. 14/161,658, filed on Jan. 22, 2014, now Pat. No. 9,083,010, and a continuation-in-part of application No. 13/944,211, filed on Jul. 17, 2013, now Pat. No. 9,136,065.

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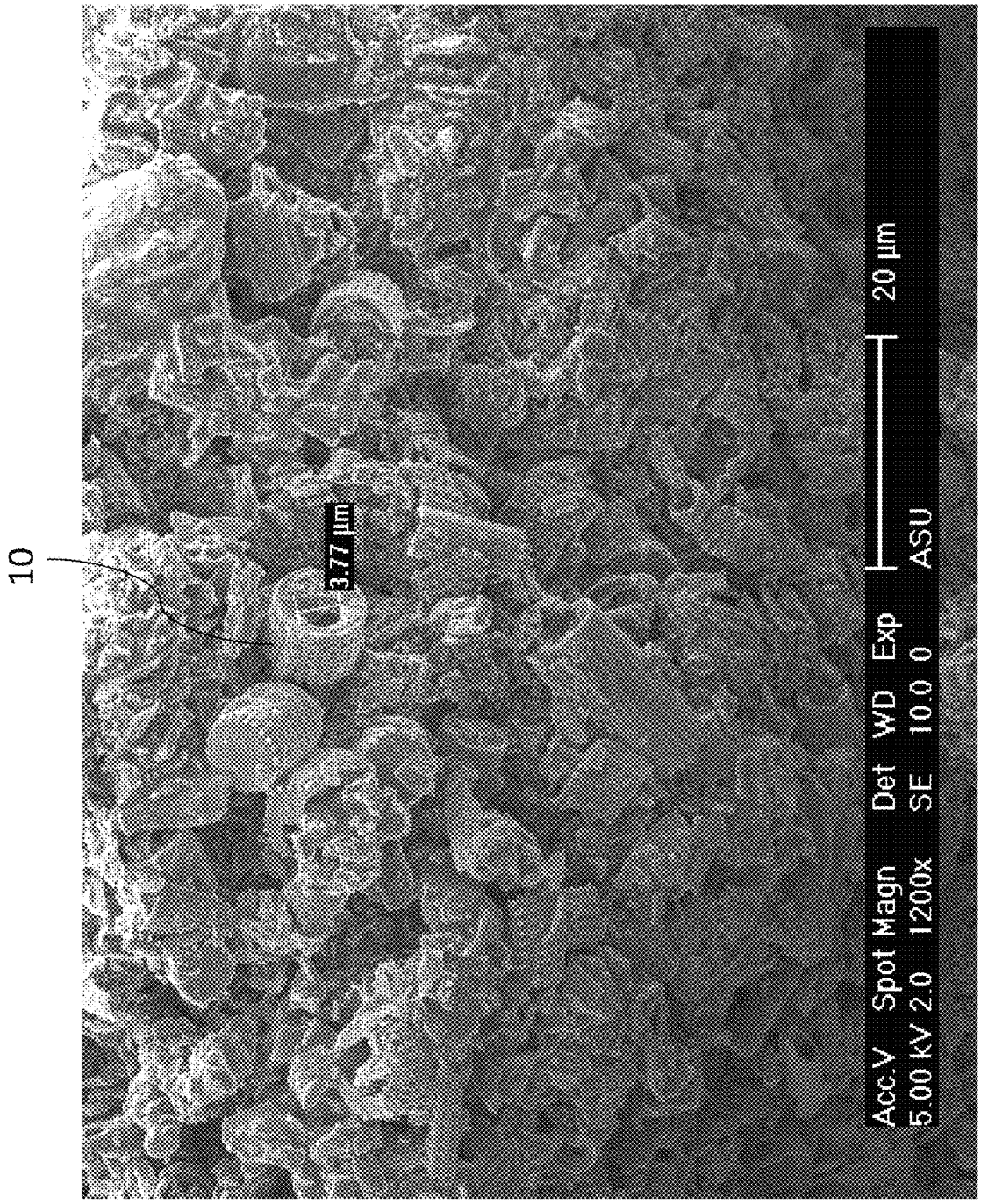

10
3.77 µm
Acc.V Spot Magn Det WD Exp
5.00 kV 2.0 1200x SE 10.0 0 ASU
20 µm

Fig. 1

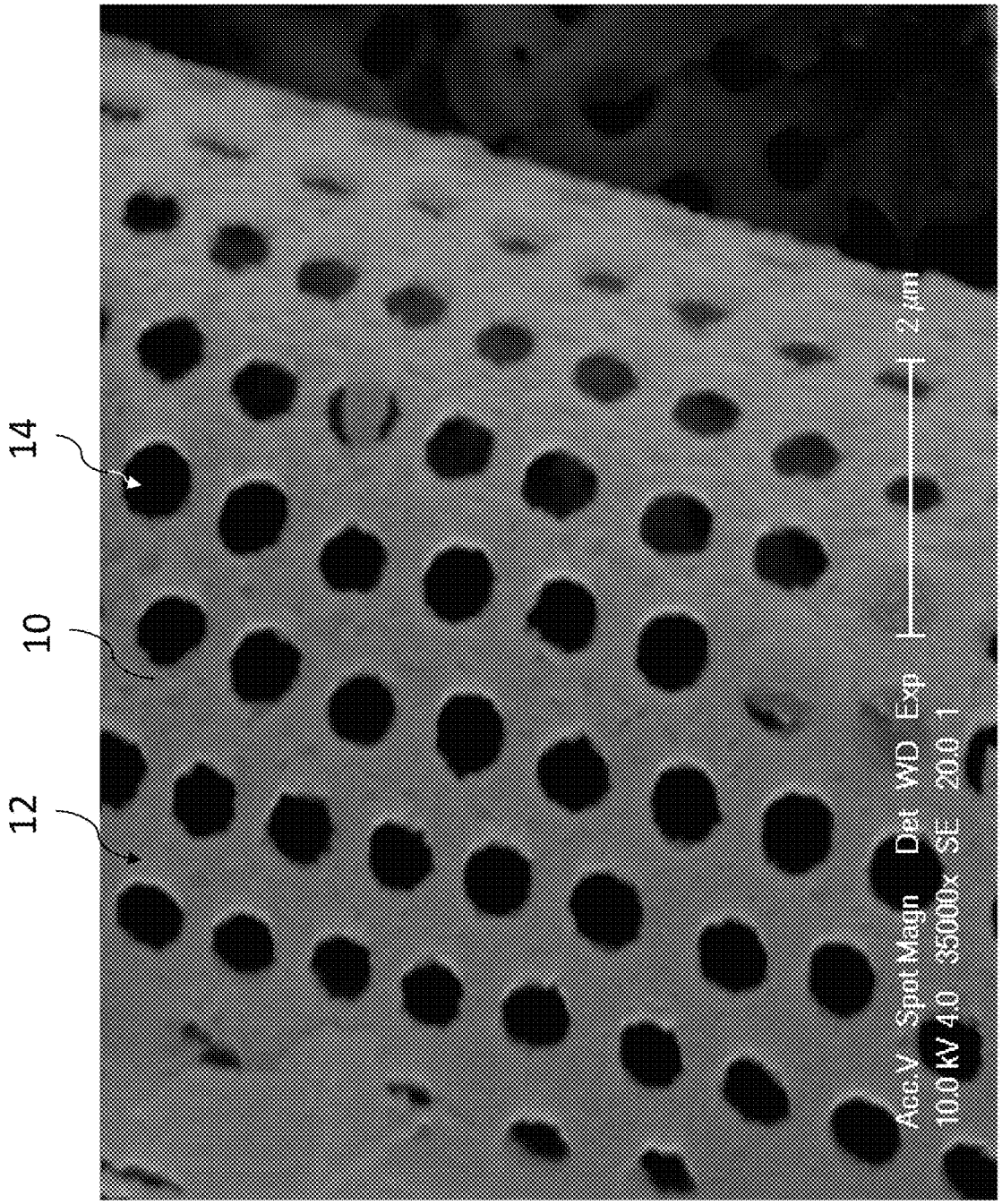


Fig. 2

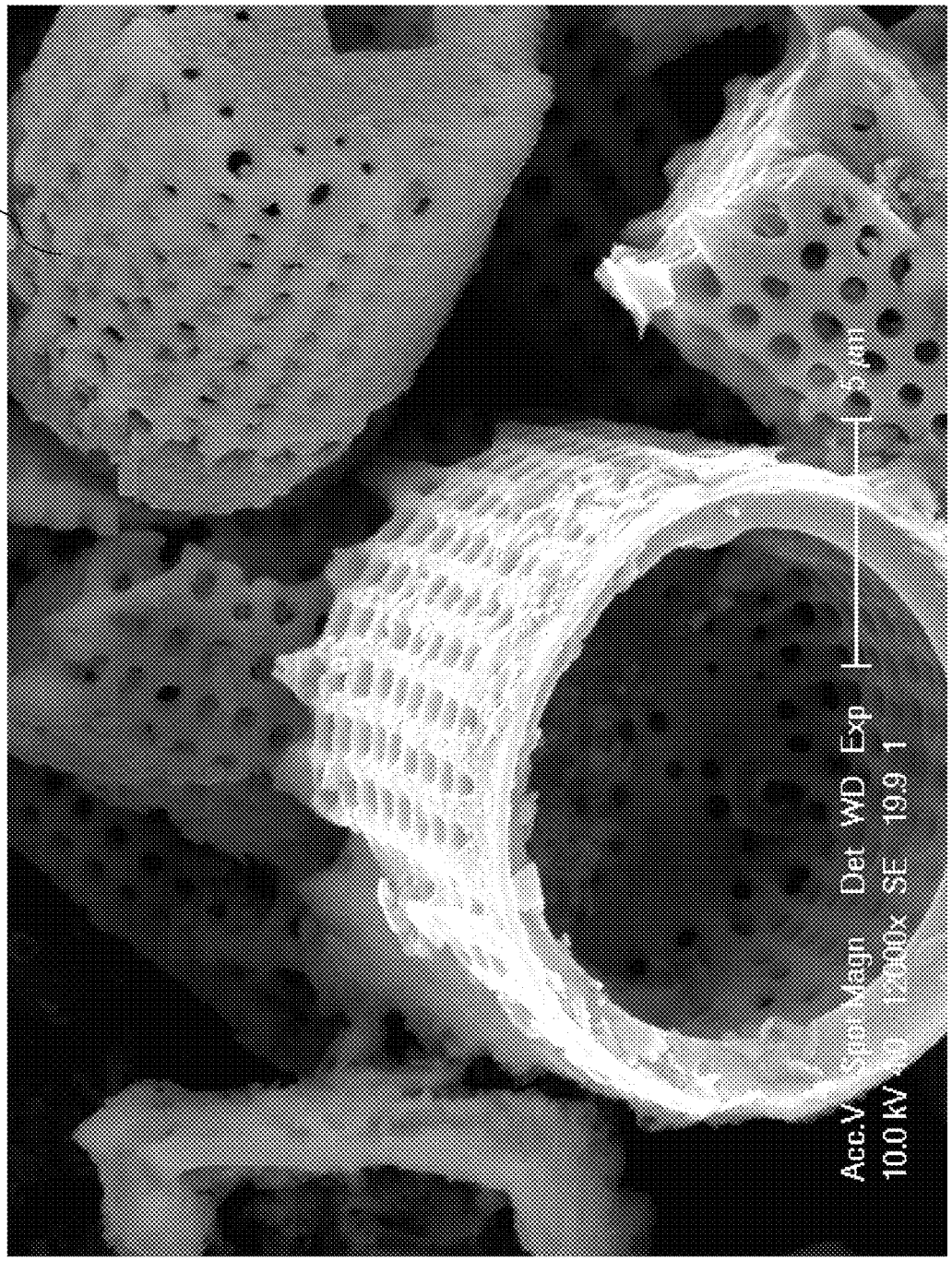


Fig. 3

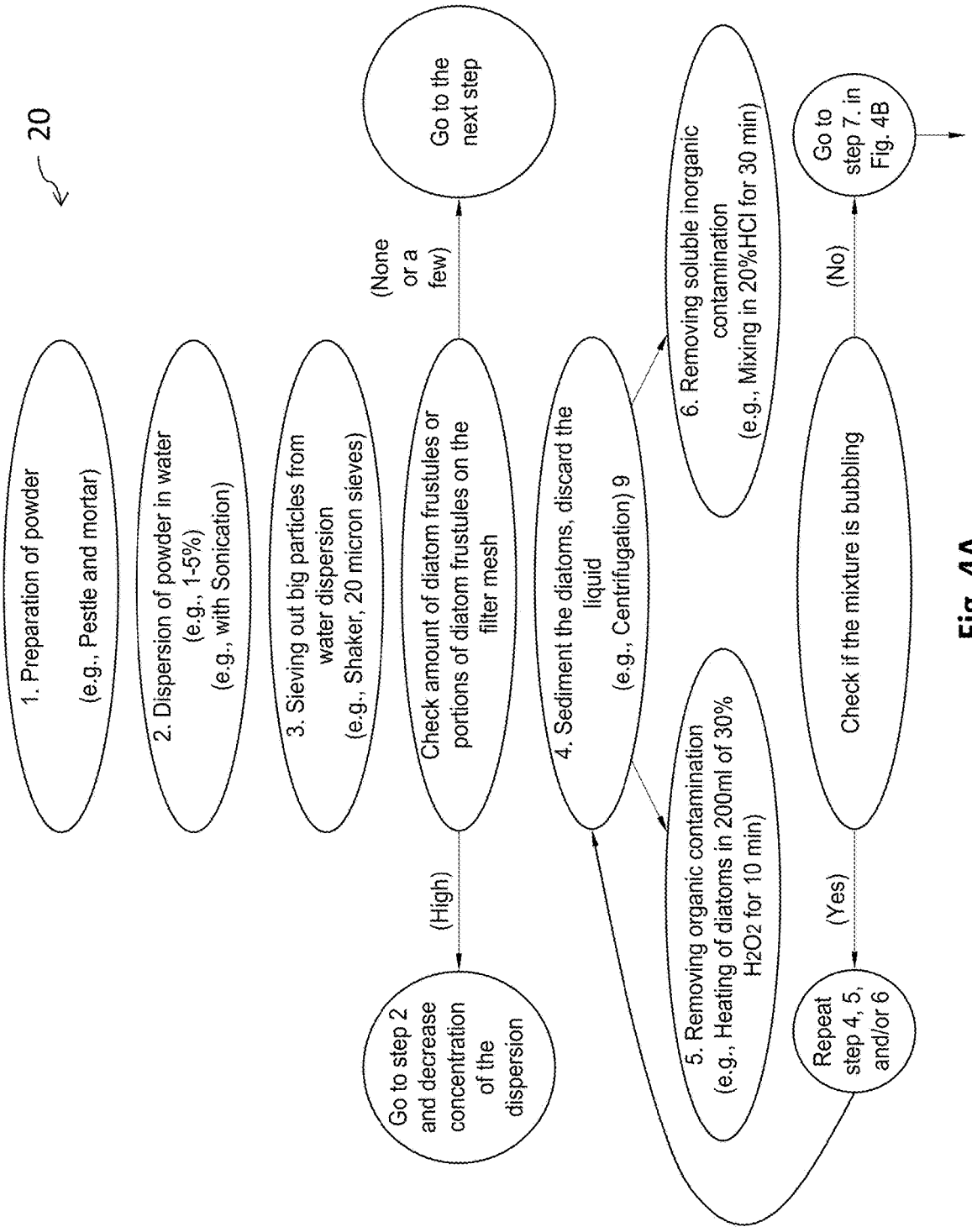

20
1. Preparation of powder
(e.g., Pestle and mortar)
2. Dispersion of powder in water
(e.g., 1-5%)
(e.g., with Sonication)
3. Sieving out big particles from water dispersion
(e.g., Shaker, 20 micron sieves)
Check amount of diatom frustules or portions of diatom frustules on the filter mesh
(None or a few)
Go to the next step
(High)
Go to step 2 and decrease concentration of the dispersion
4. Sediment the diatoms, discard the liquid
(e.g., Centrifugation) 9
5. Removing organic contamination
(e.g., Heating of diatoms in 200ml of 30% H2O2 for 10 min)
6. Removing soluble inorganic contamination
(e.g., Mixing in 20%HCl for 30 min)
Check if the mixture is bubbling
(Yes)
Repeat step 4, 5, and/or 6
(No)
Go to step 7. in Fig. 4B

Fig. 4A

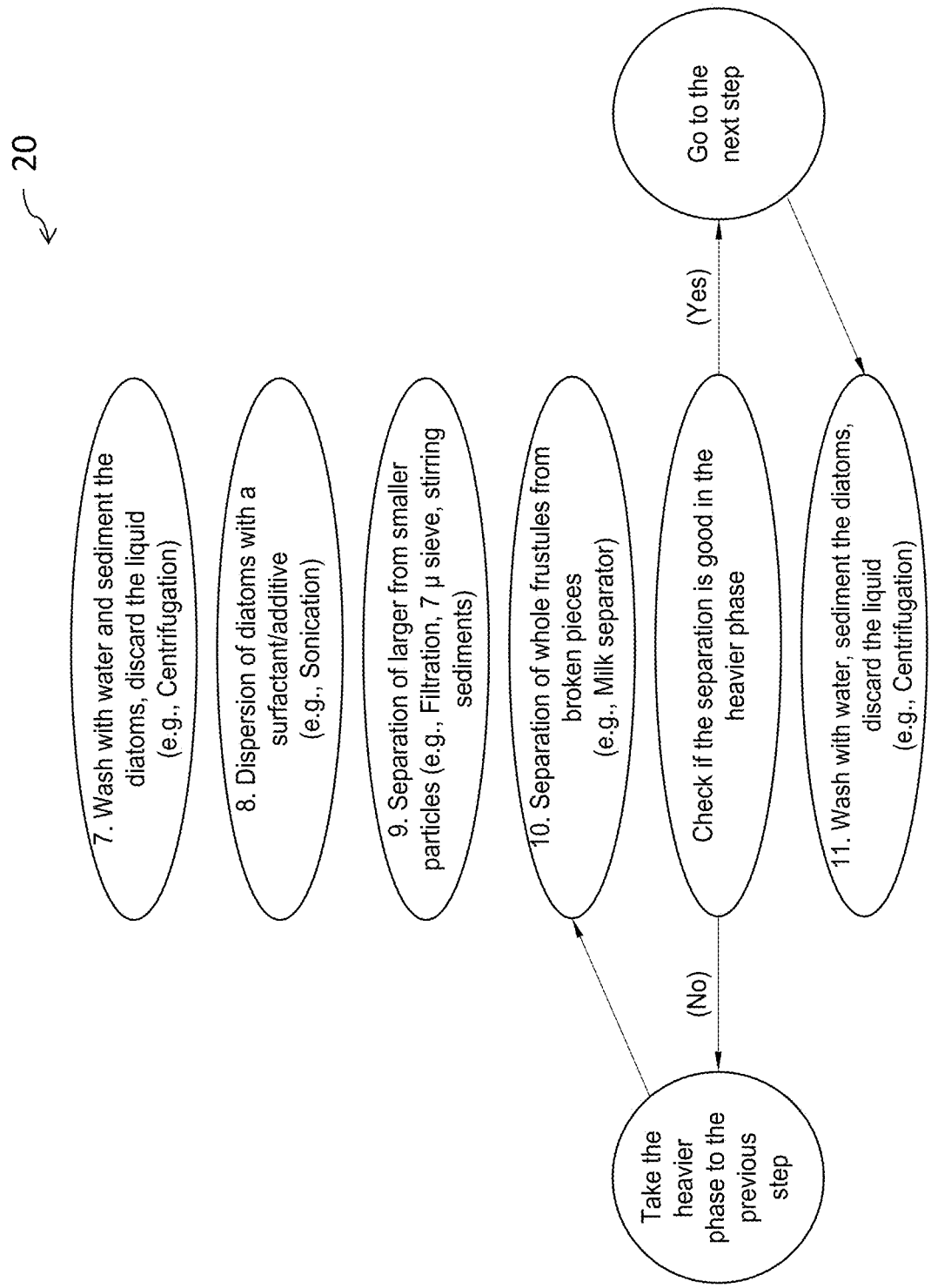

20
7. Wash with water and sediment the diatoms, discard the liquid (e.g., Centrifugation)
8. Dispersion of diatoms with a surfactant/additive (e.g., Sonication)
9. Separation of larger from smaller particles (e.g., Filtration, 7 μ sieve, stirring sediments)
10. Separation of whole frustules from broken pieces (e.g., Milk separator)
Check if the separation is good in the heavier phase
11. Wash with water, sediment the diatoms, discard the liquid (e.g., Centrifugation)
(Yes)
Go to the next step
(No)
Take the heavier phase to the previous step

Fig. 4B

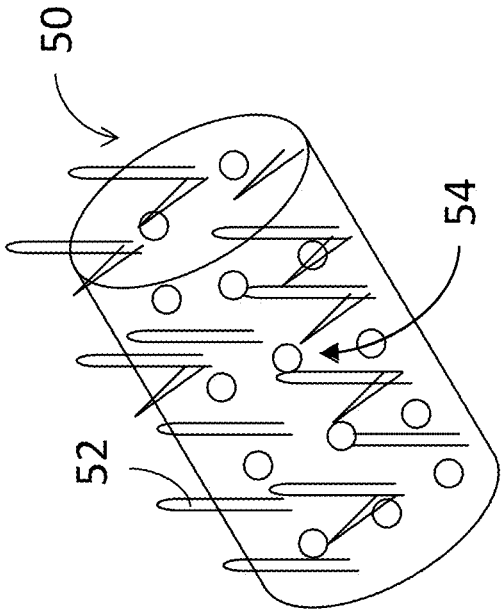


Fig. 5A

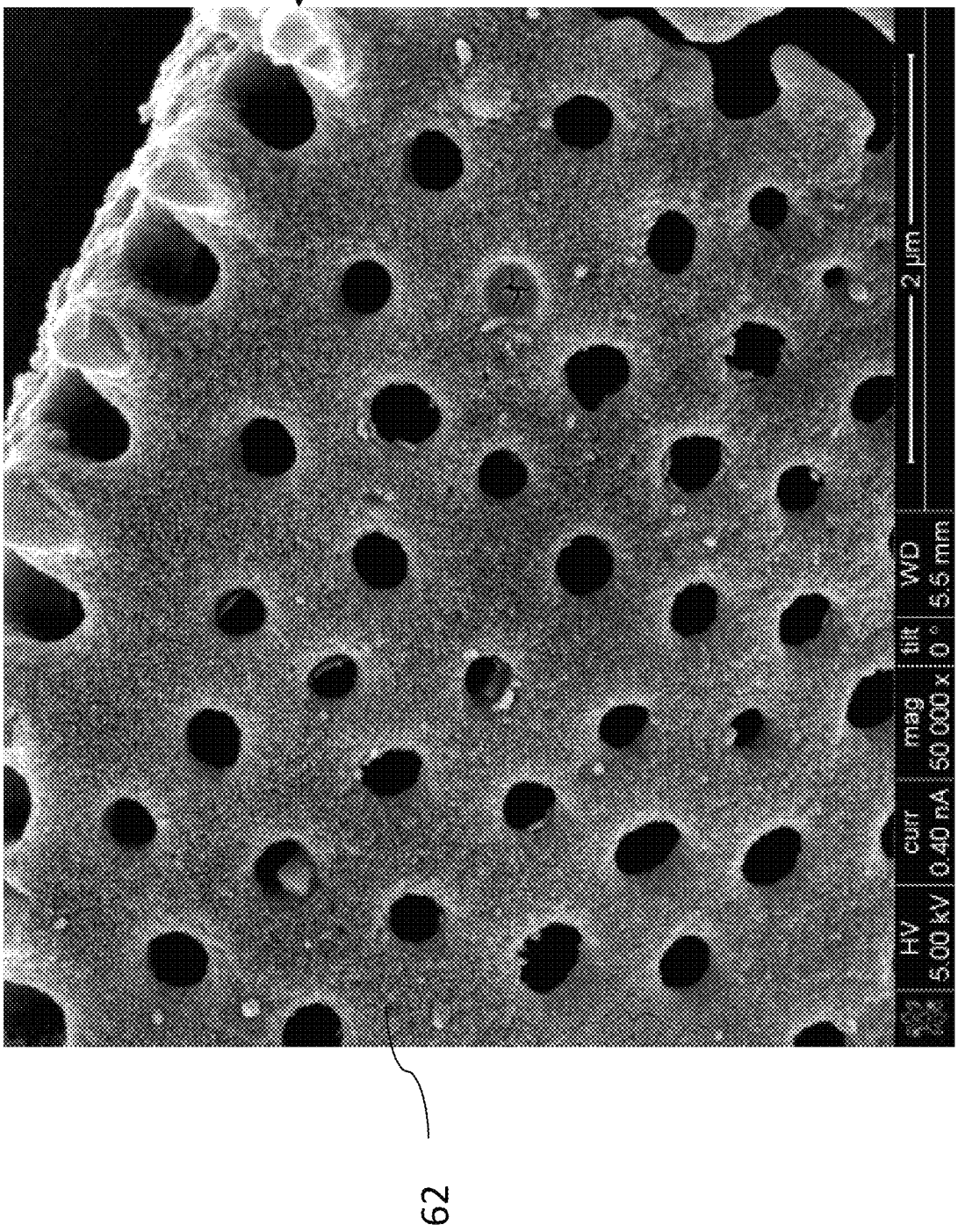


Fig. 5B

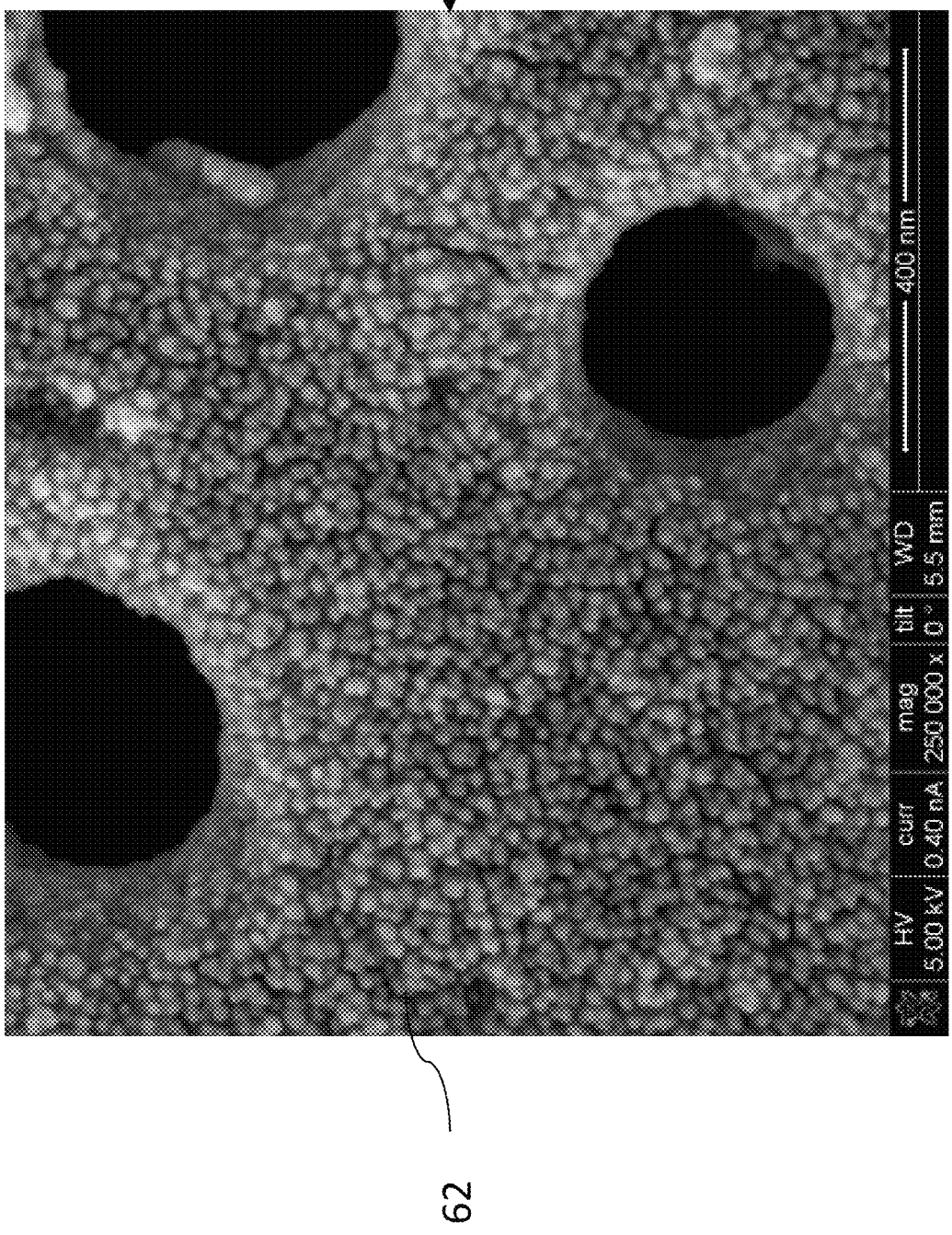


Fig. 5C

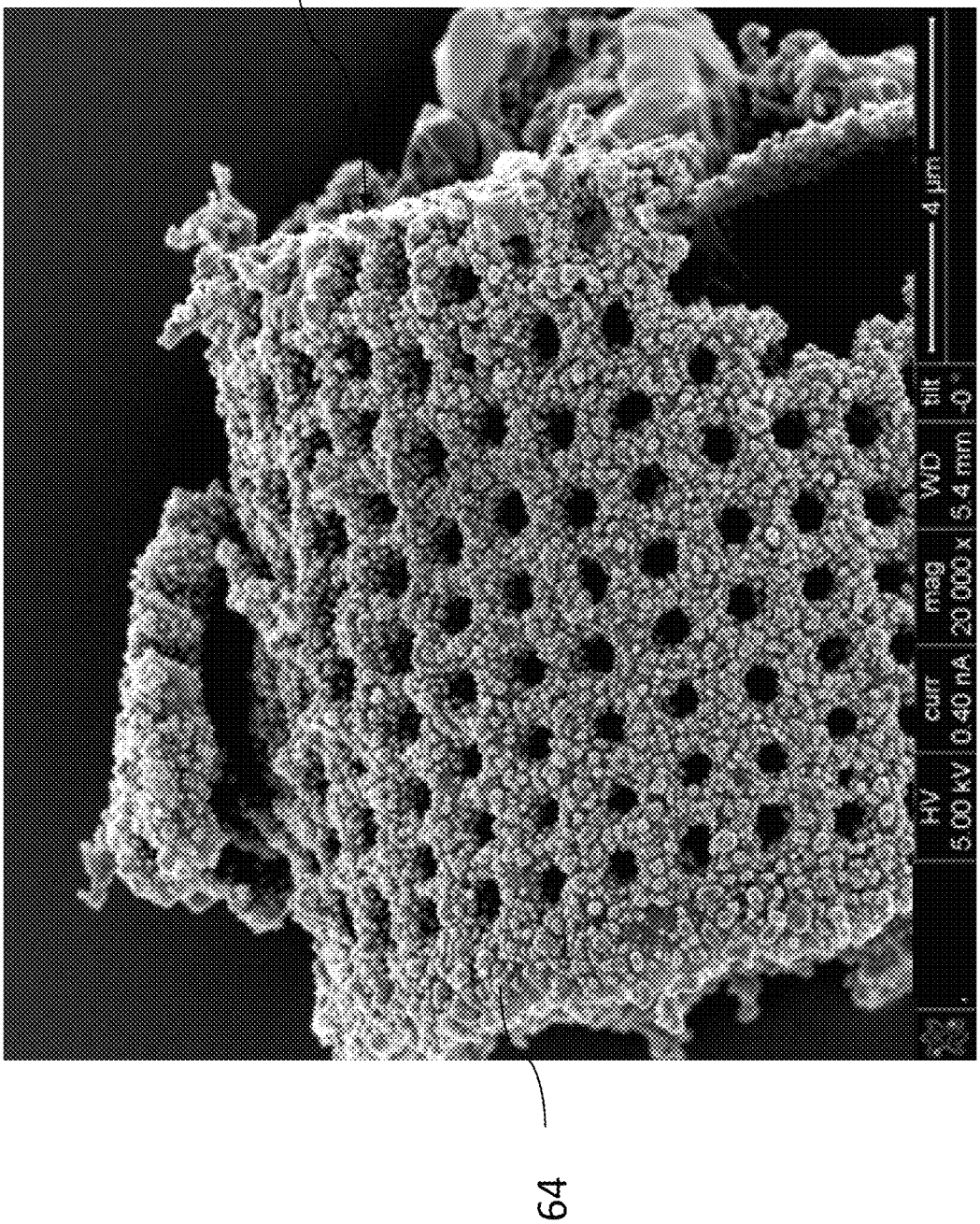


Fig. 5D

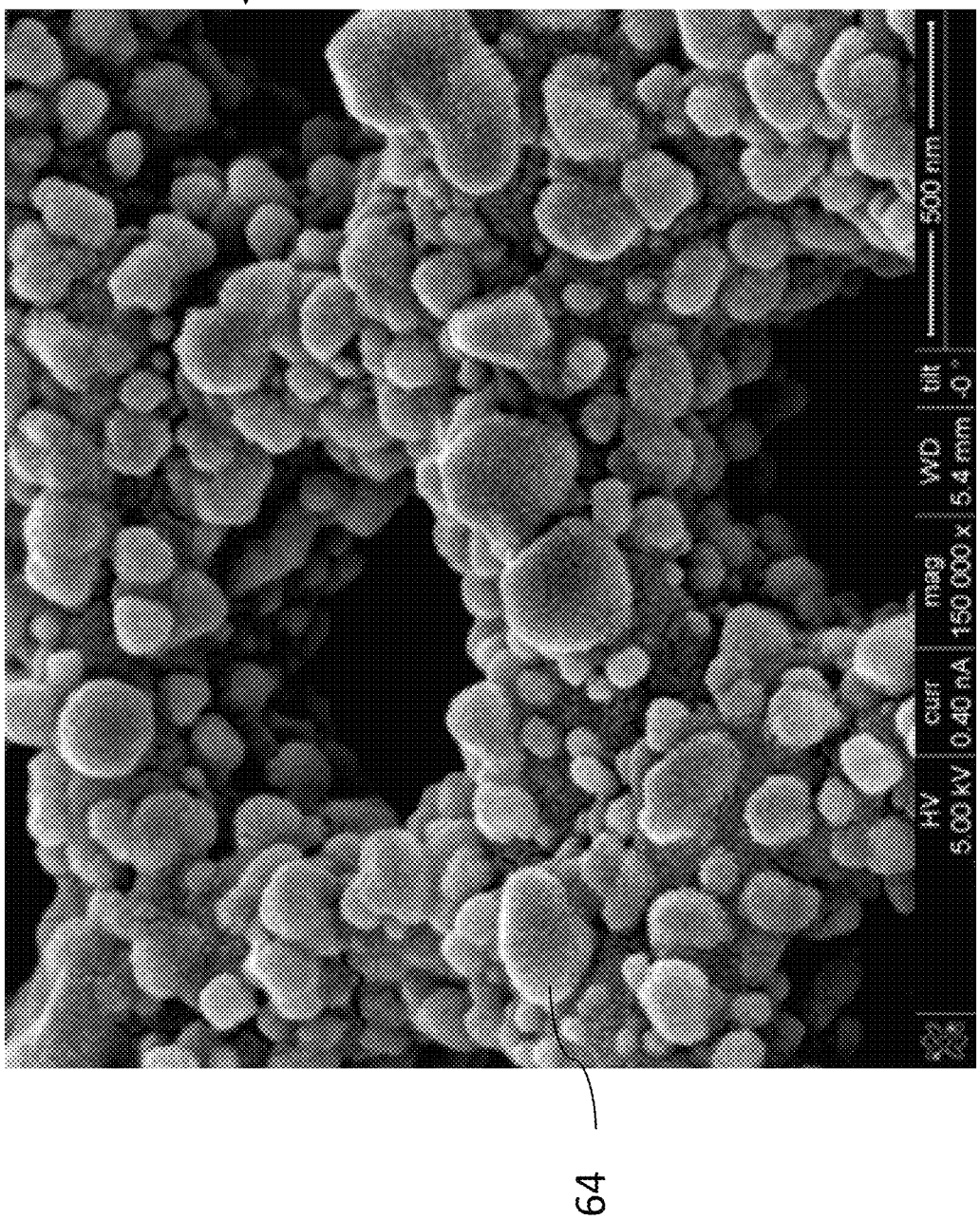


Fig. 5E

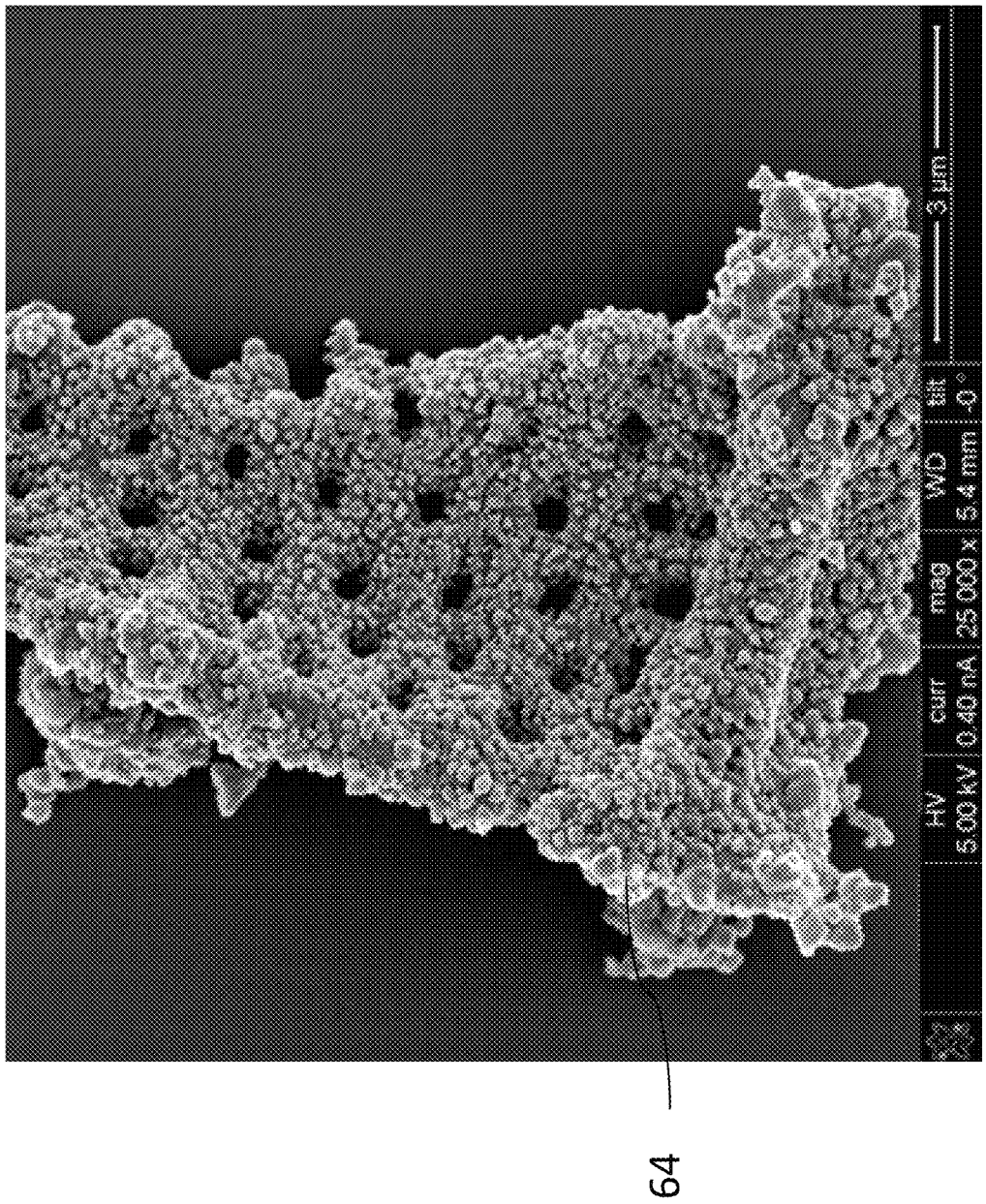


Fig. 5F

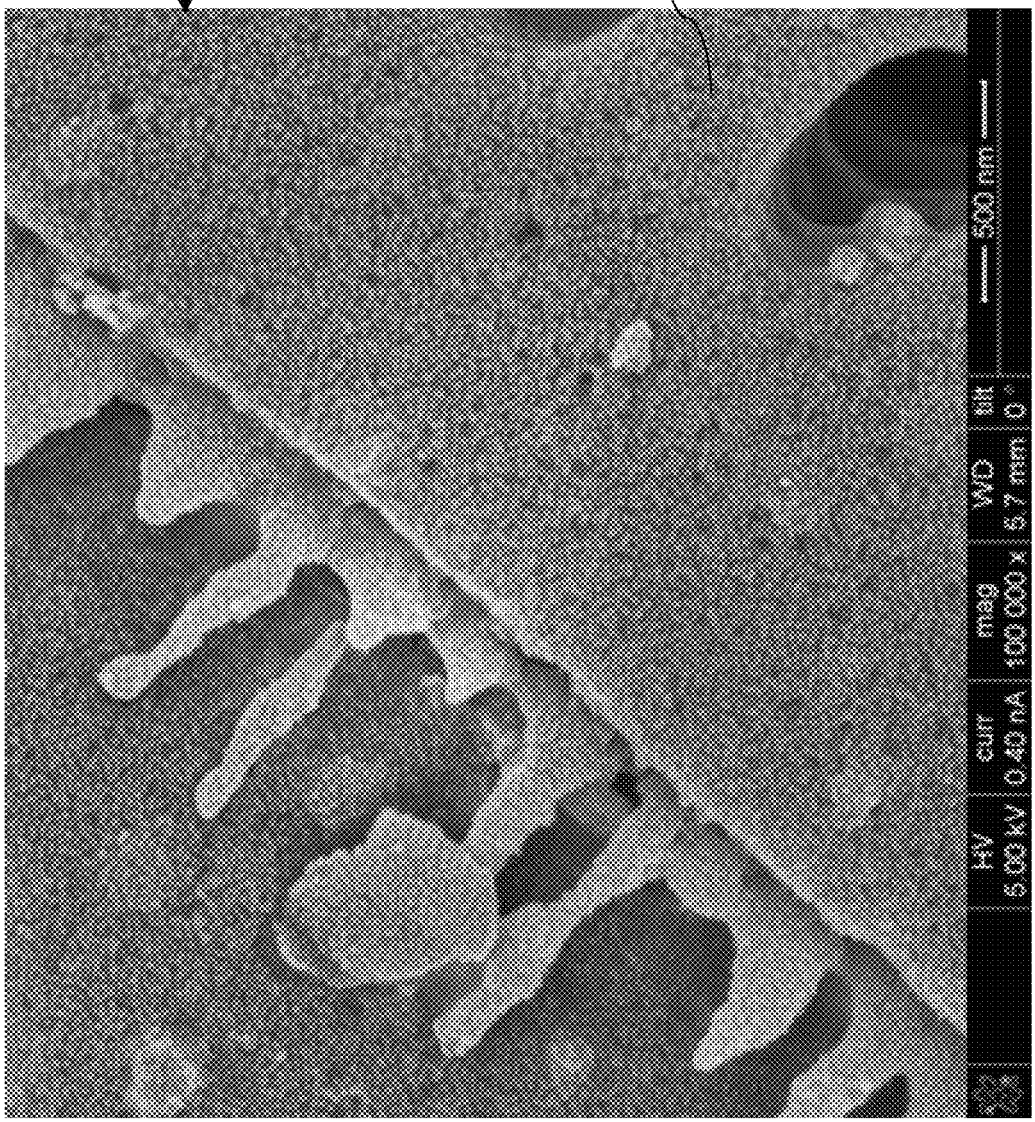


Fig. 5G

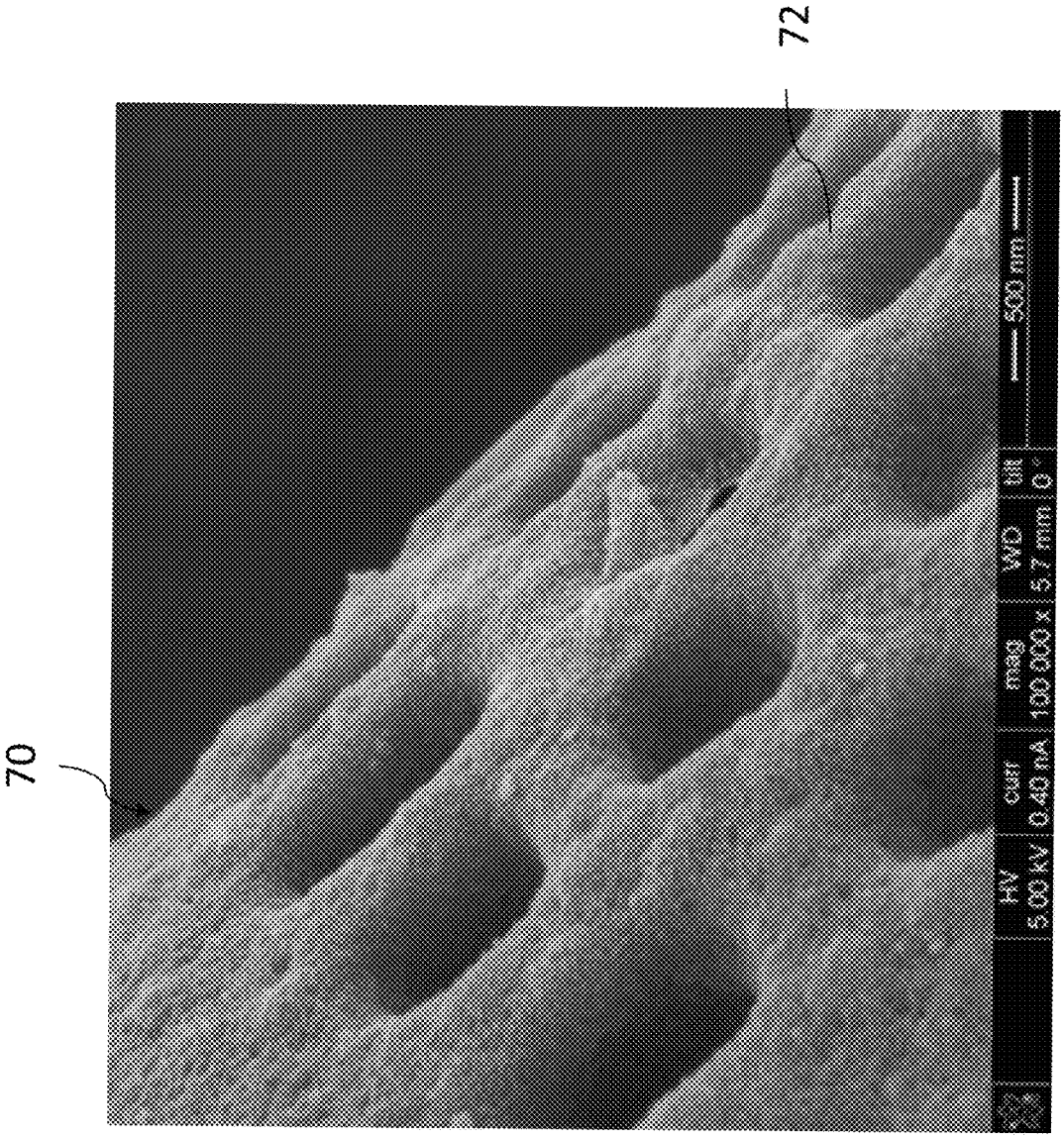


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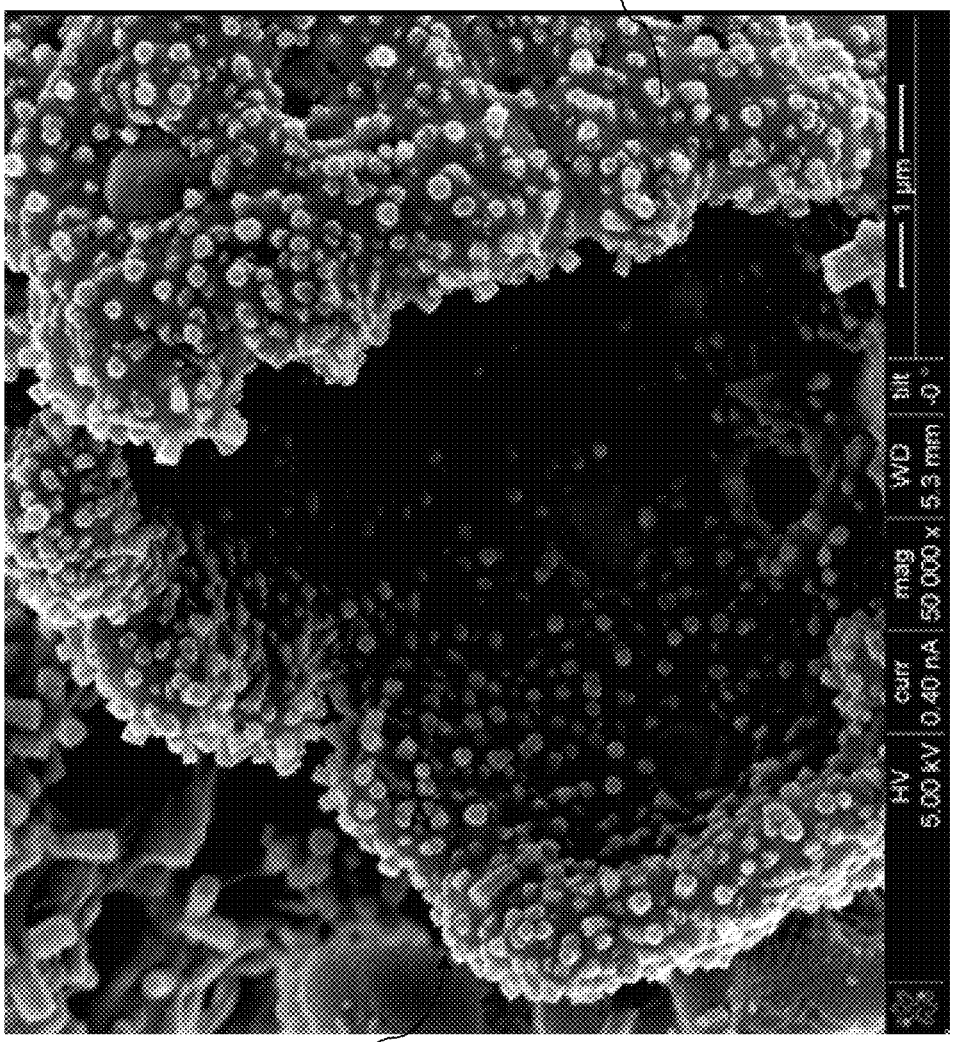


Fig. 5I

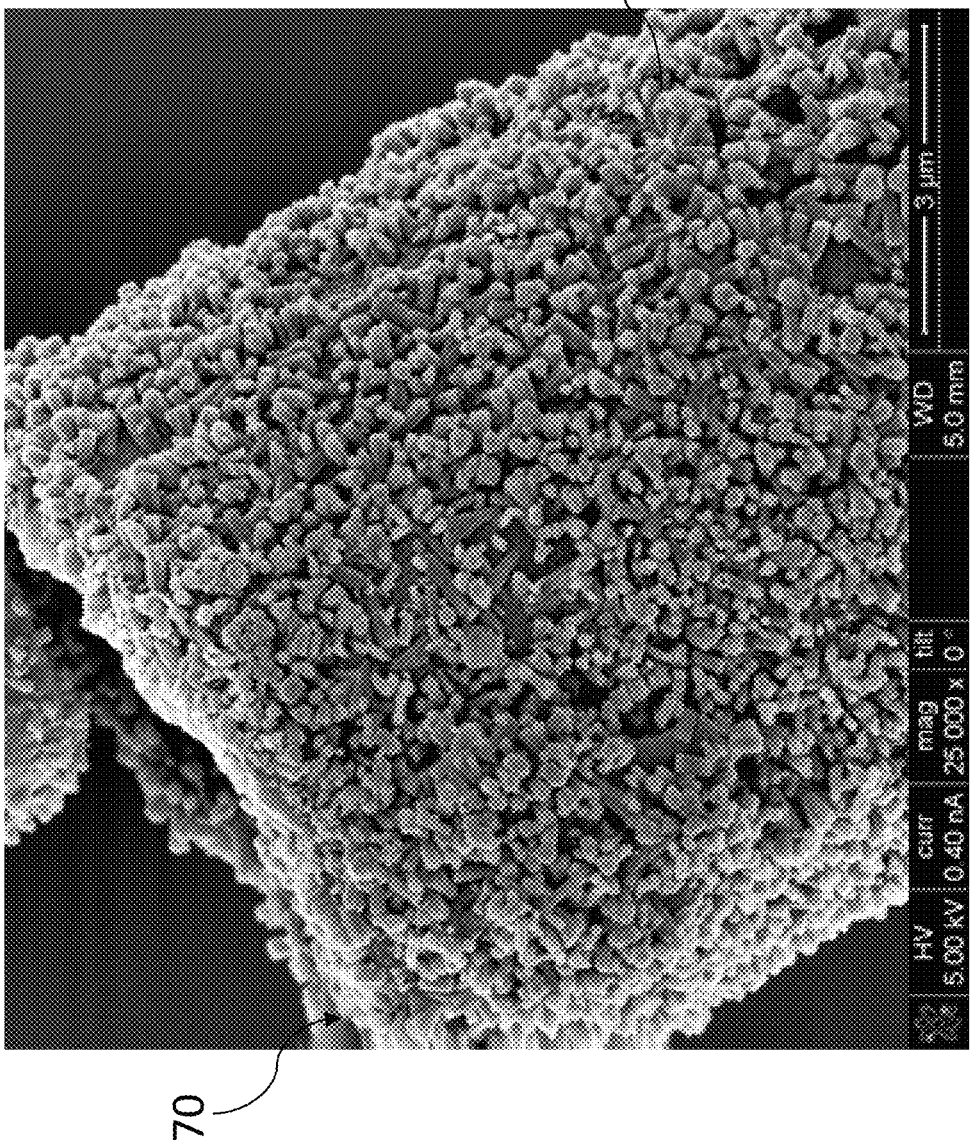


Fig. 5J

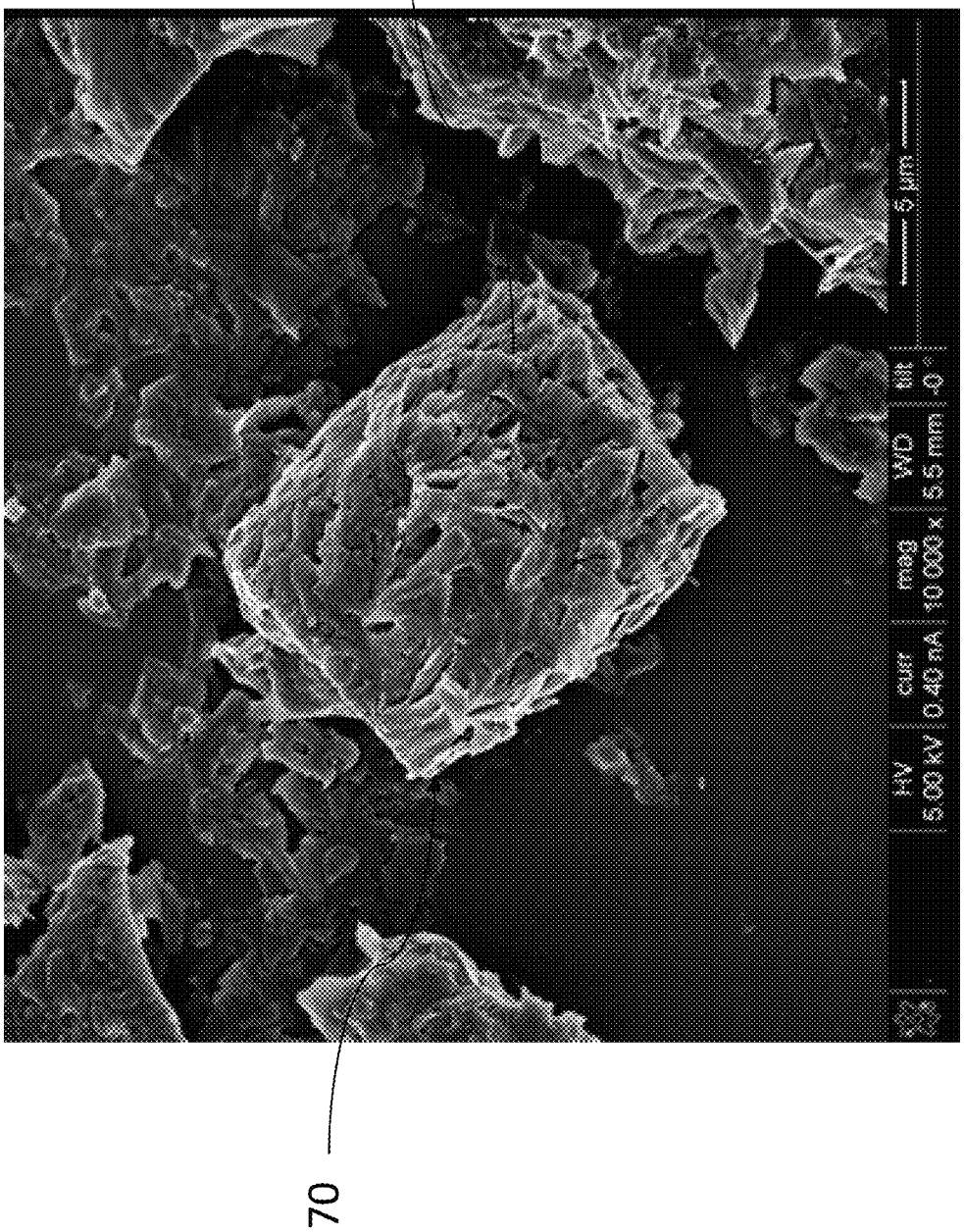


Fig. 5K

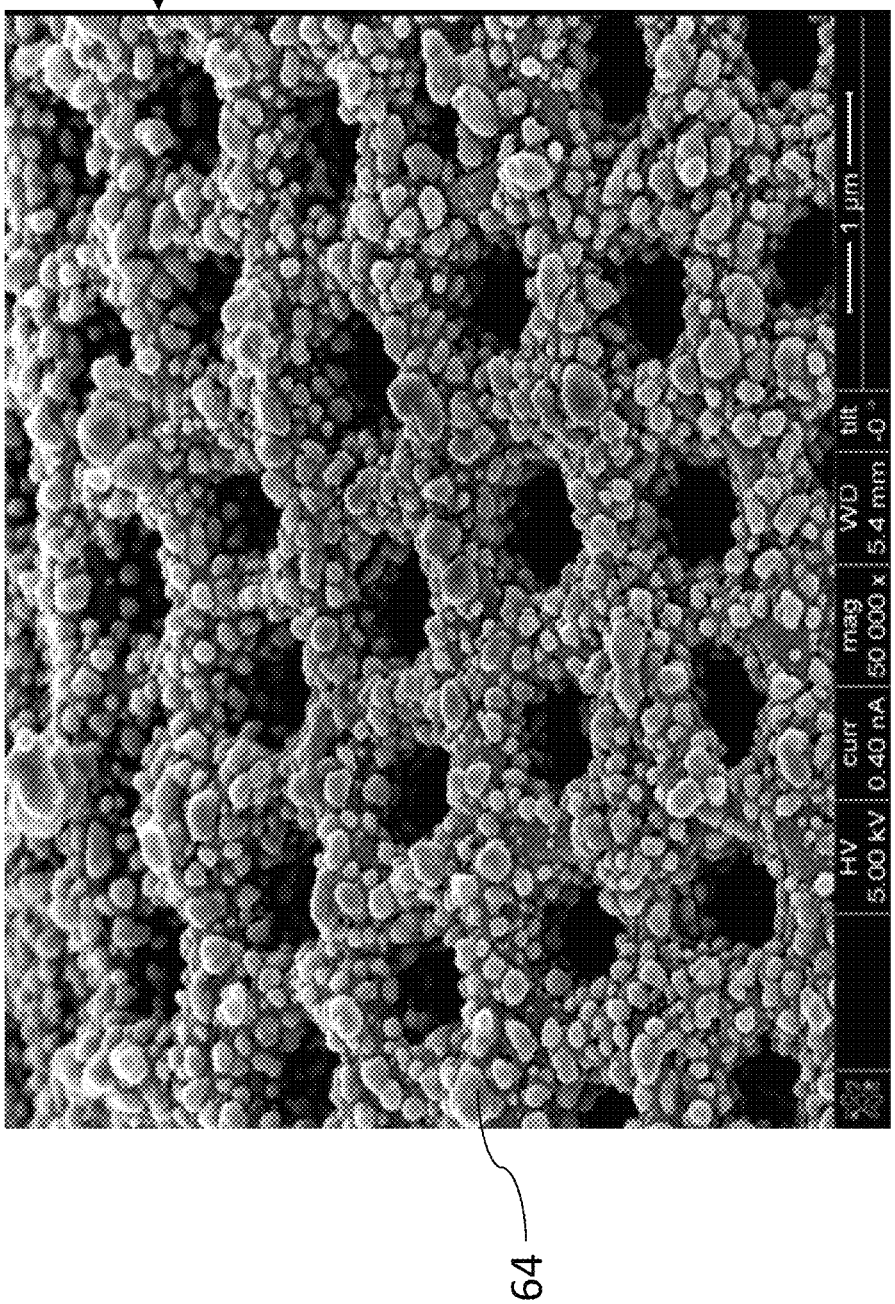


Fig. 5L

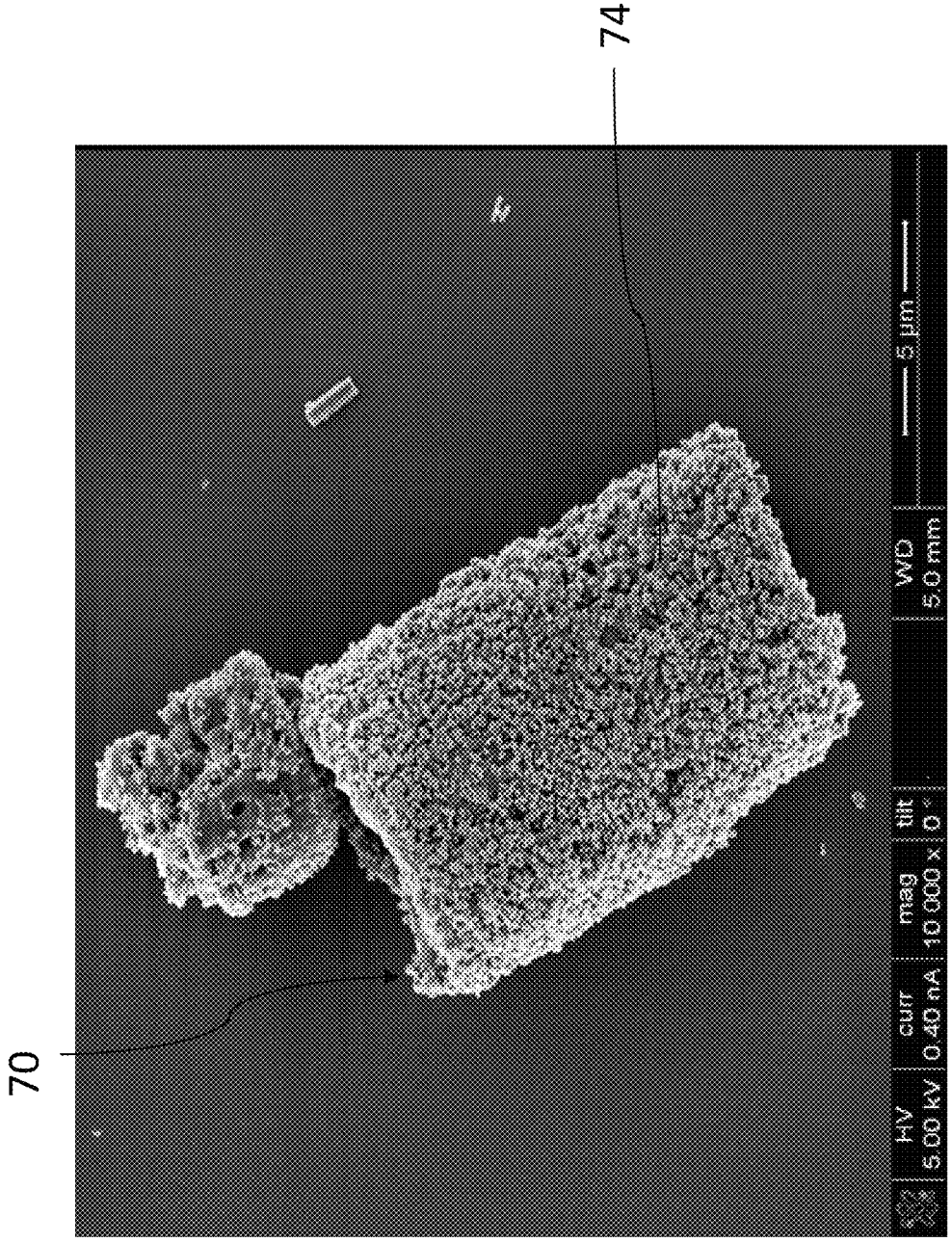


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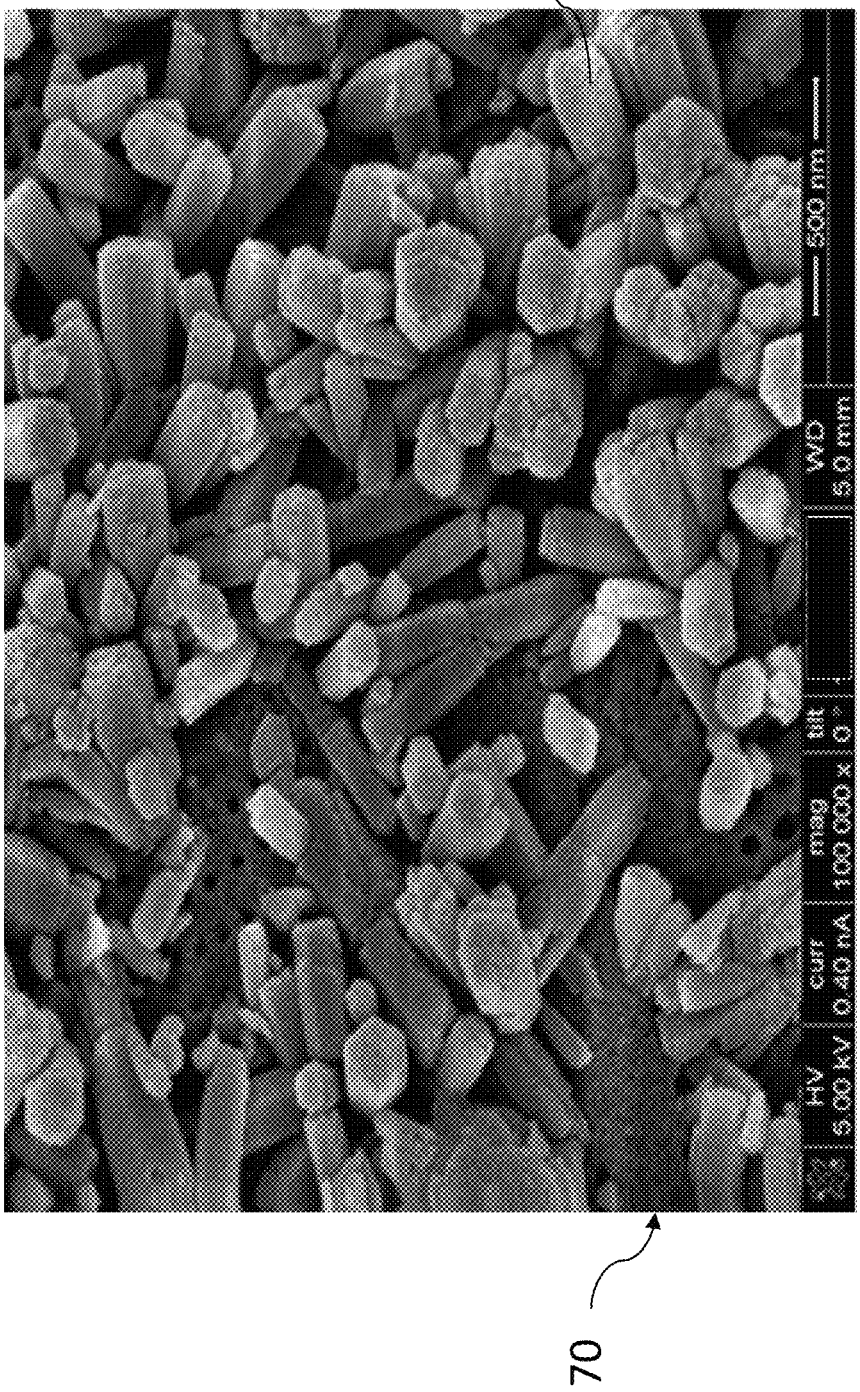


Fig. 5N

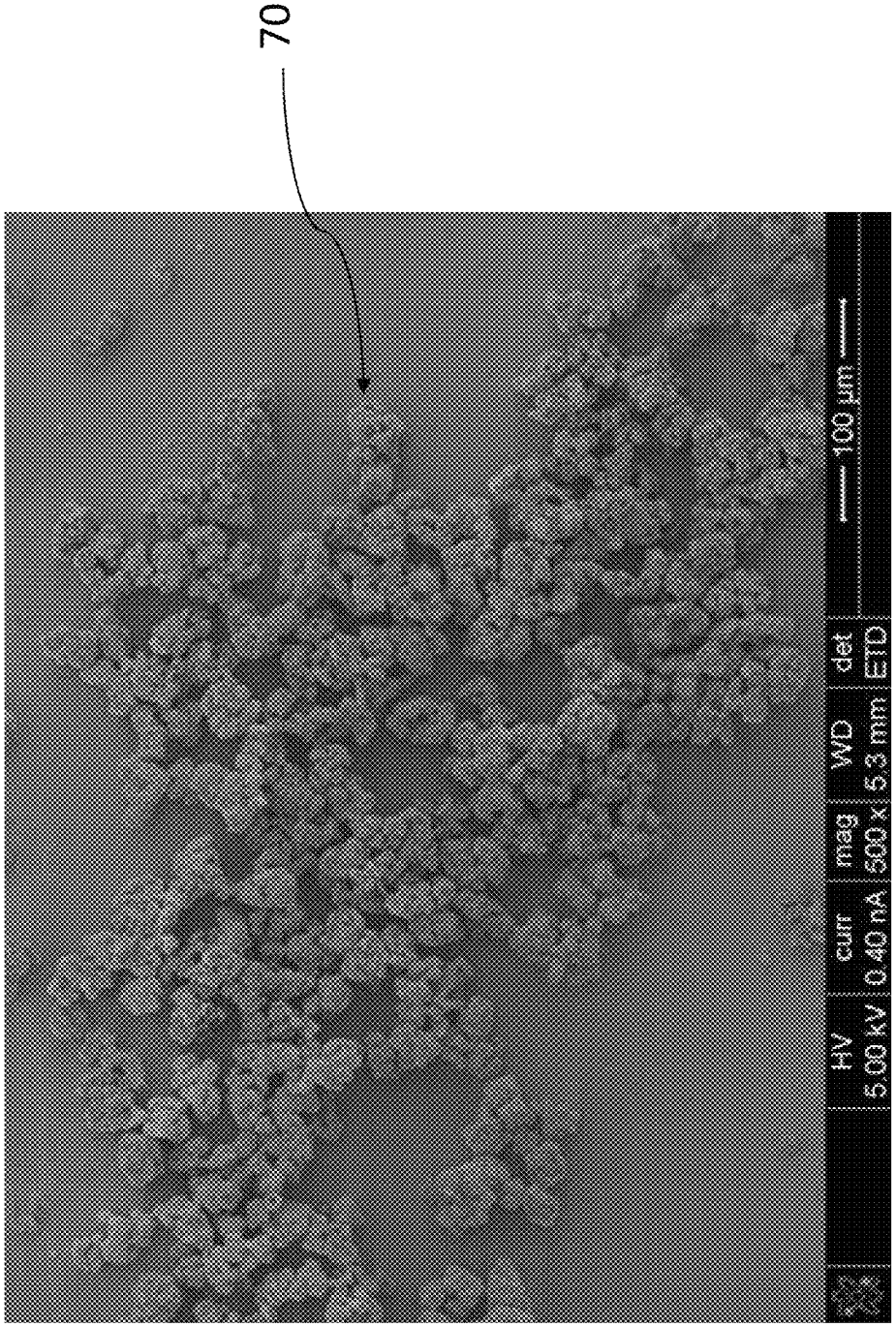


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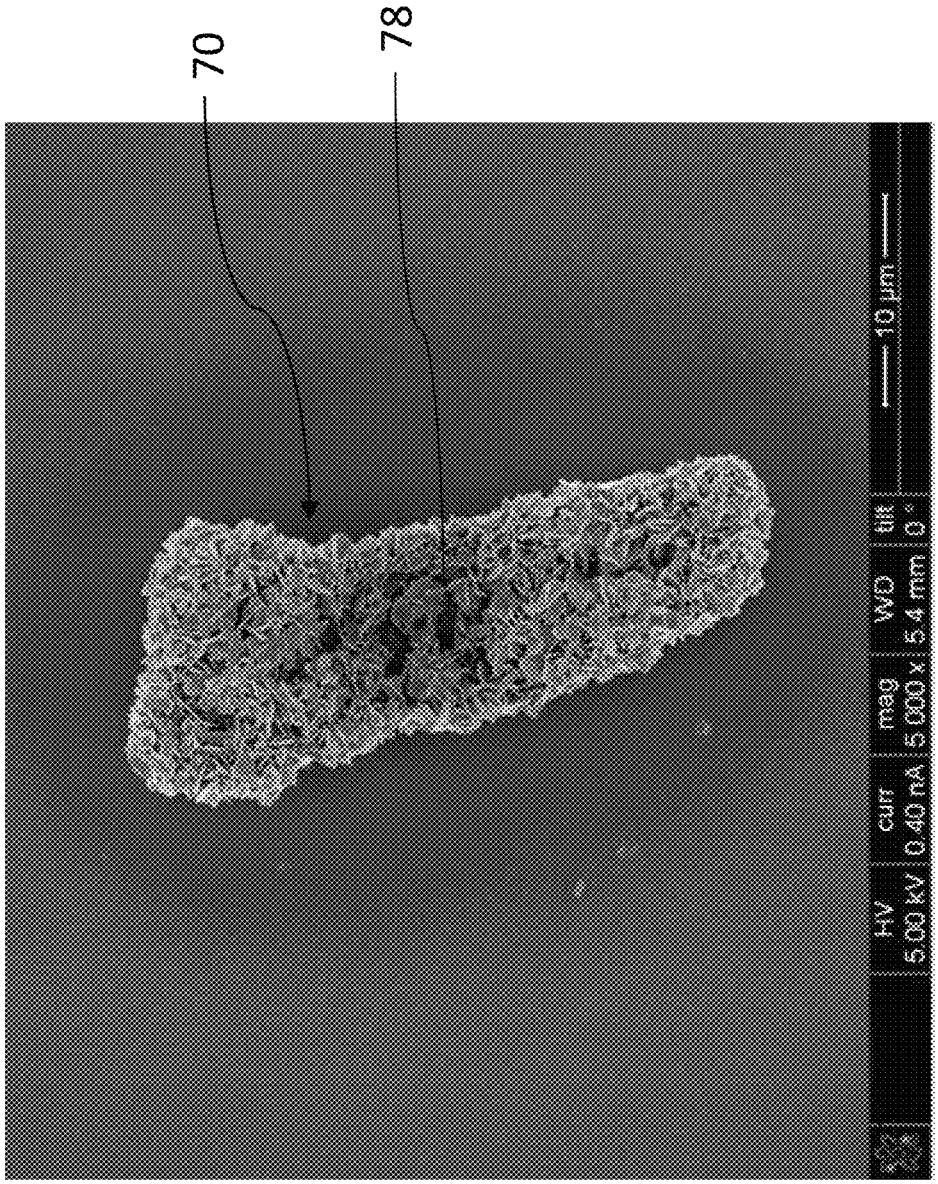


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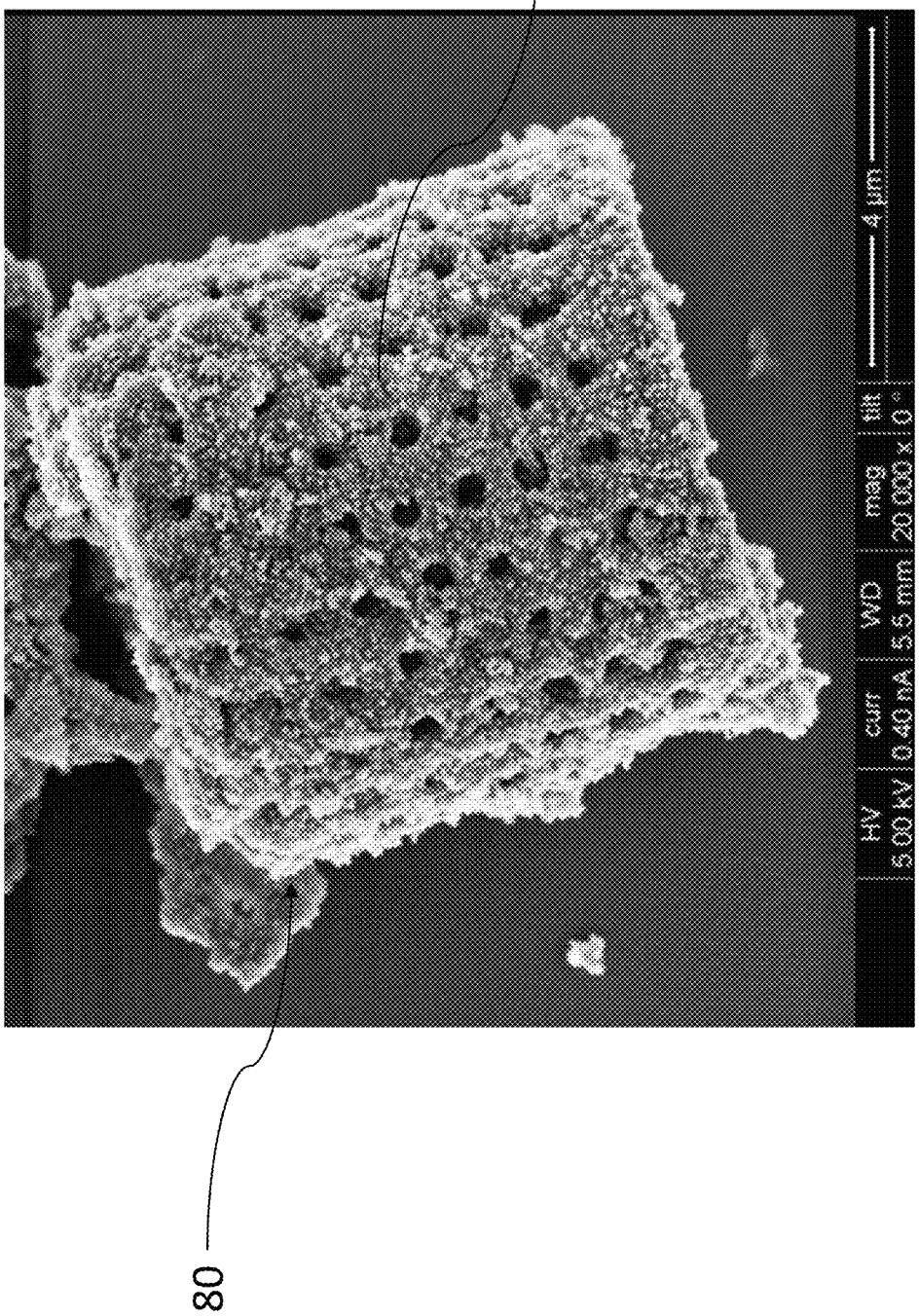


Fig. 5Q

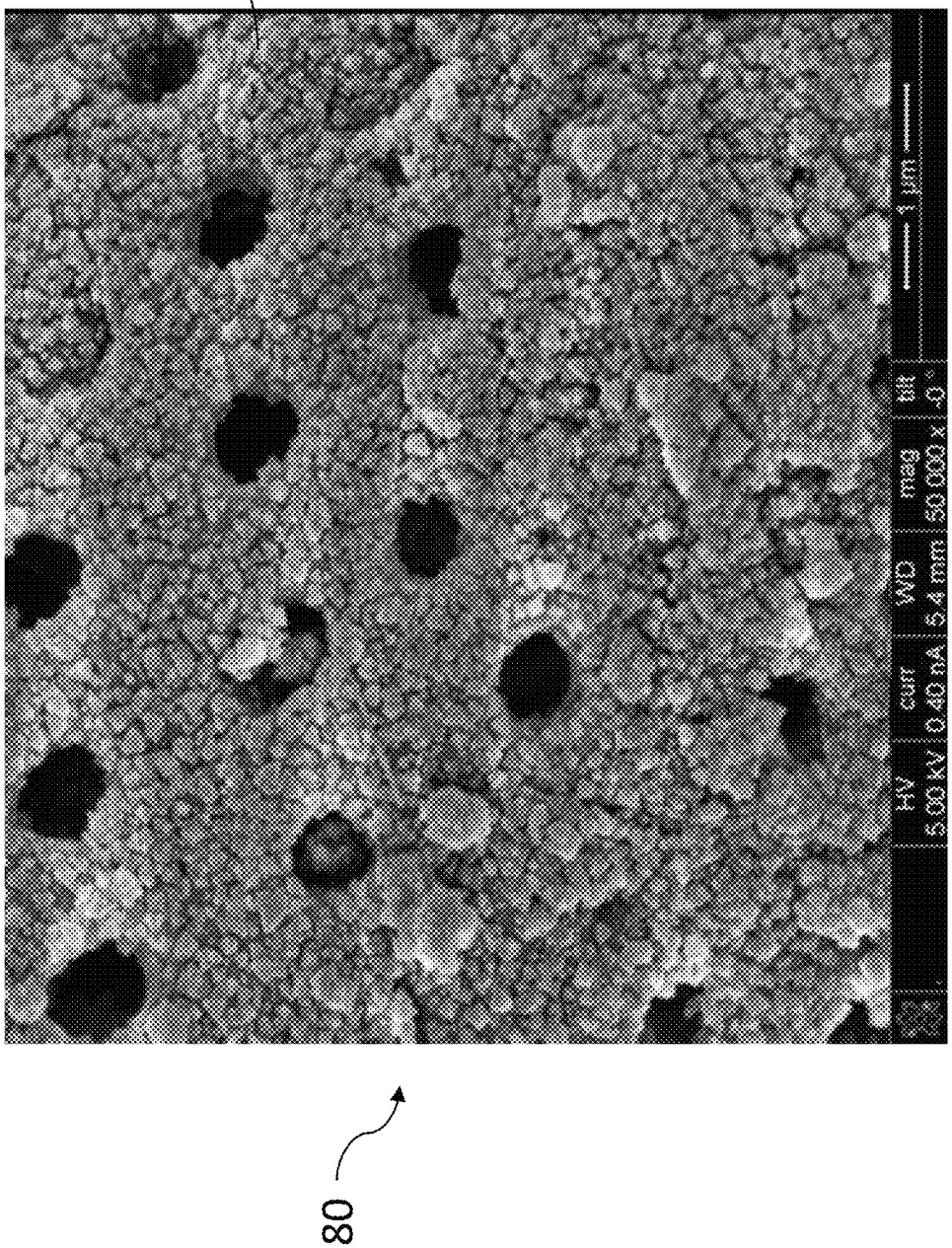


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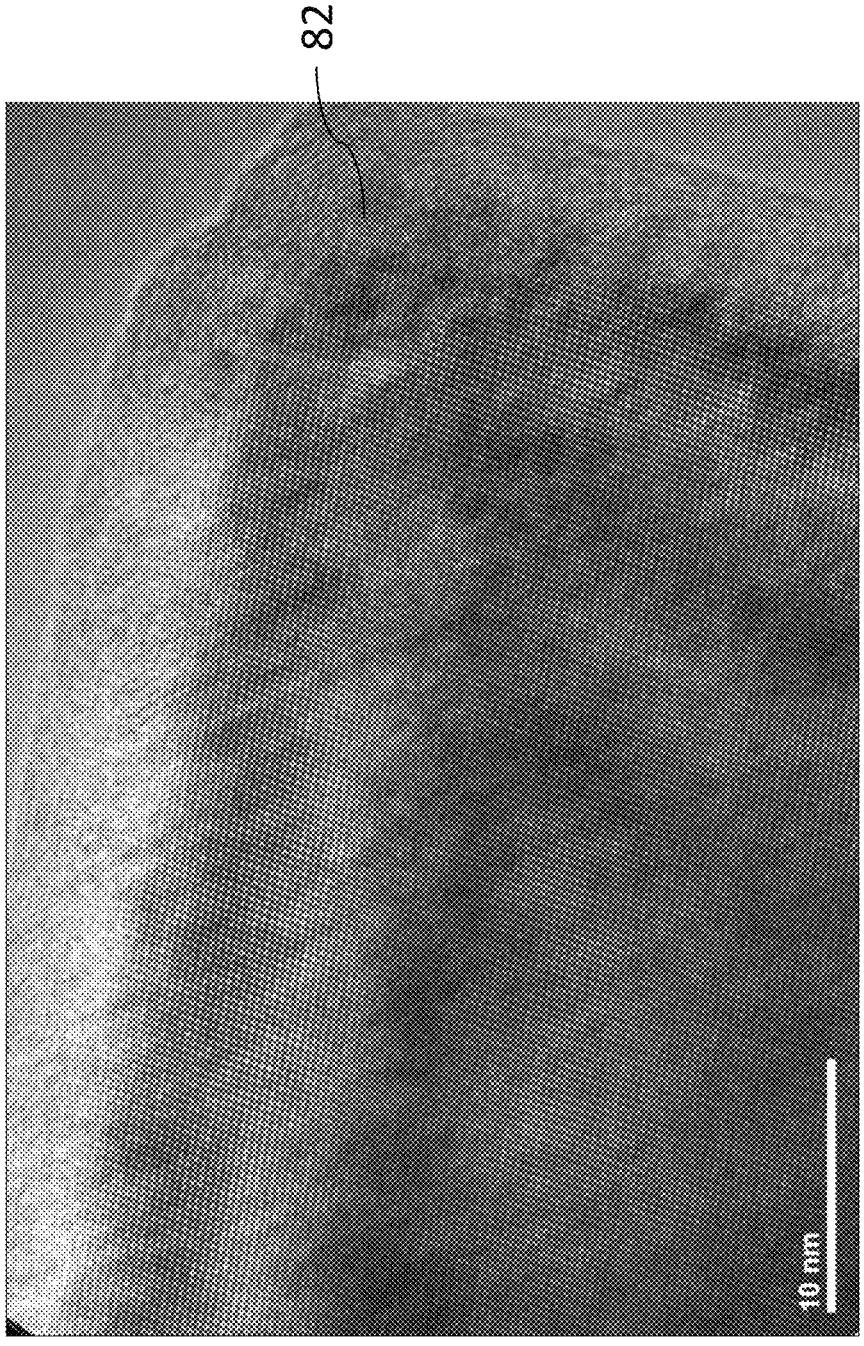


Fig. 5S

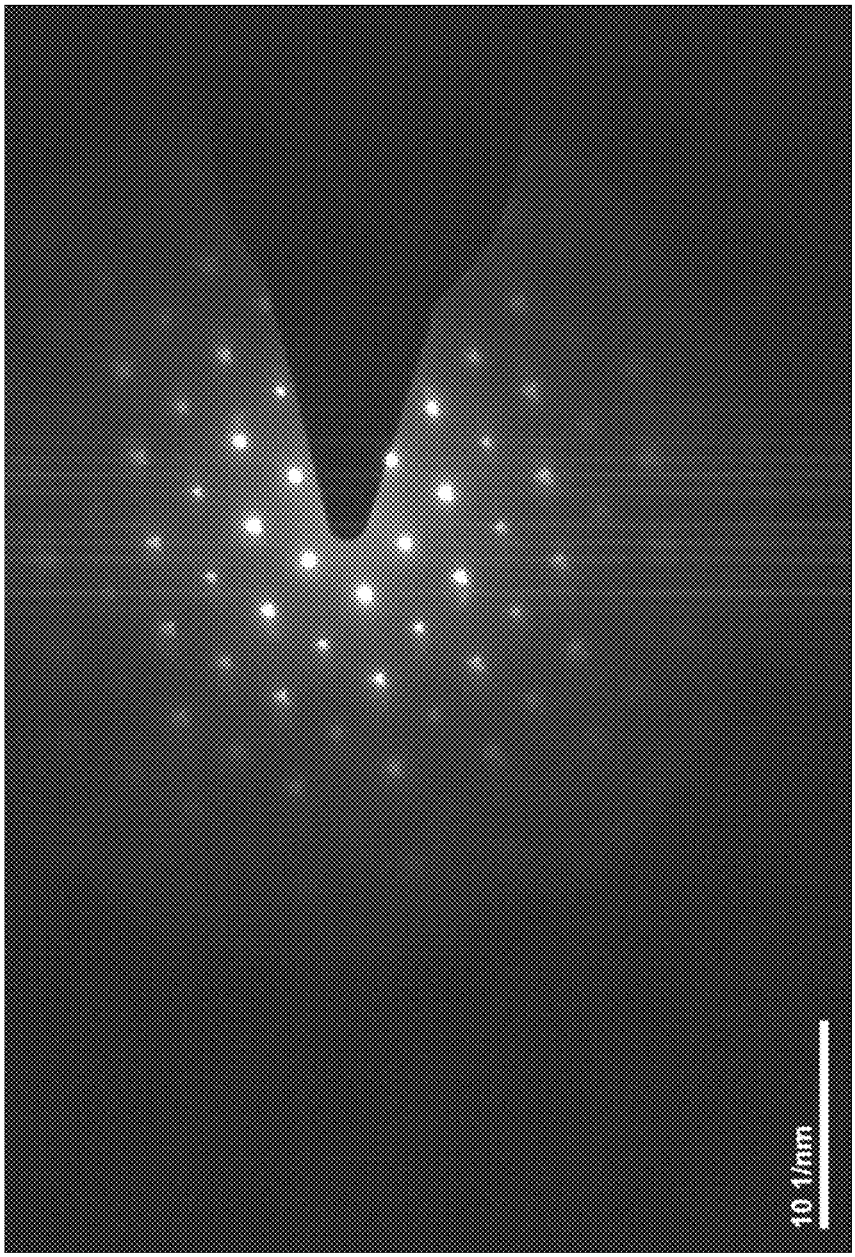


Fig. 5T

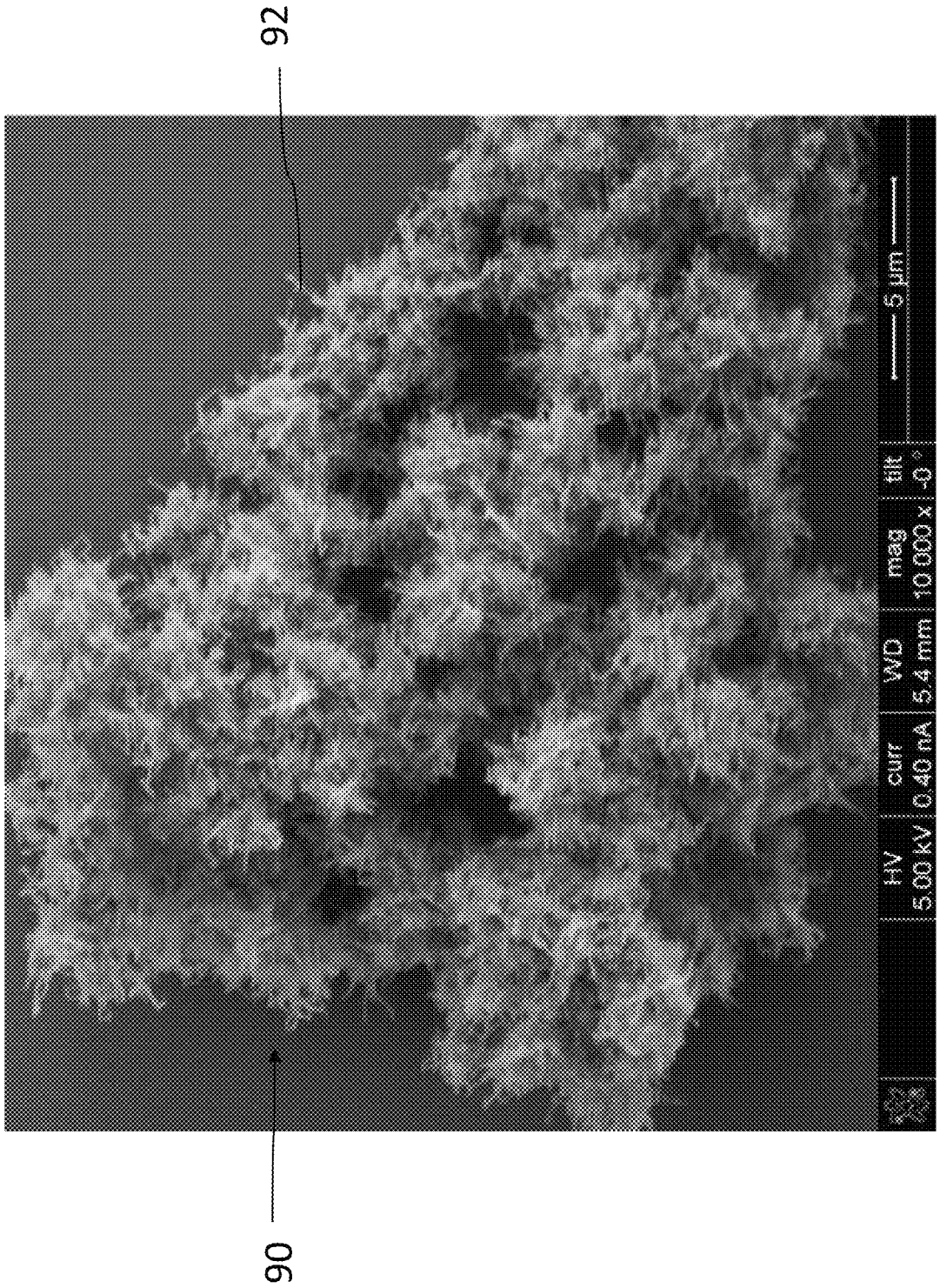


Fig. 5U

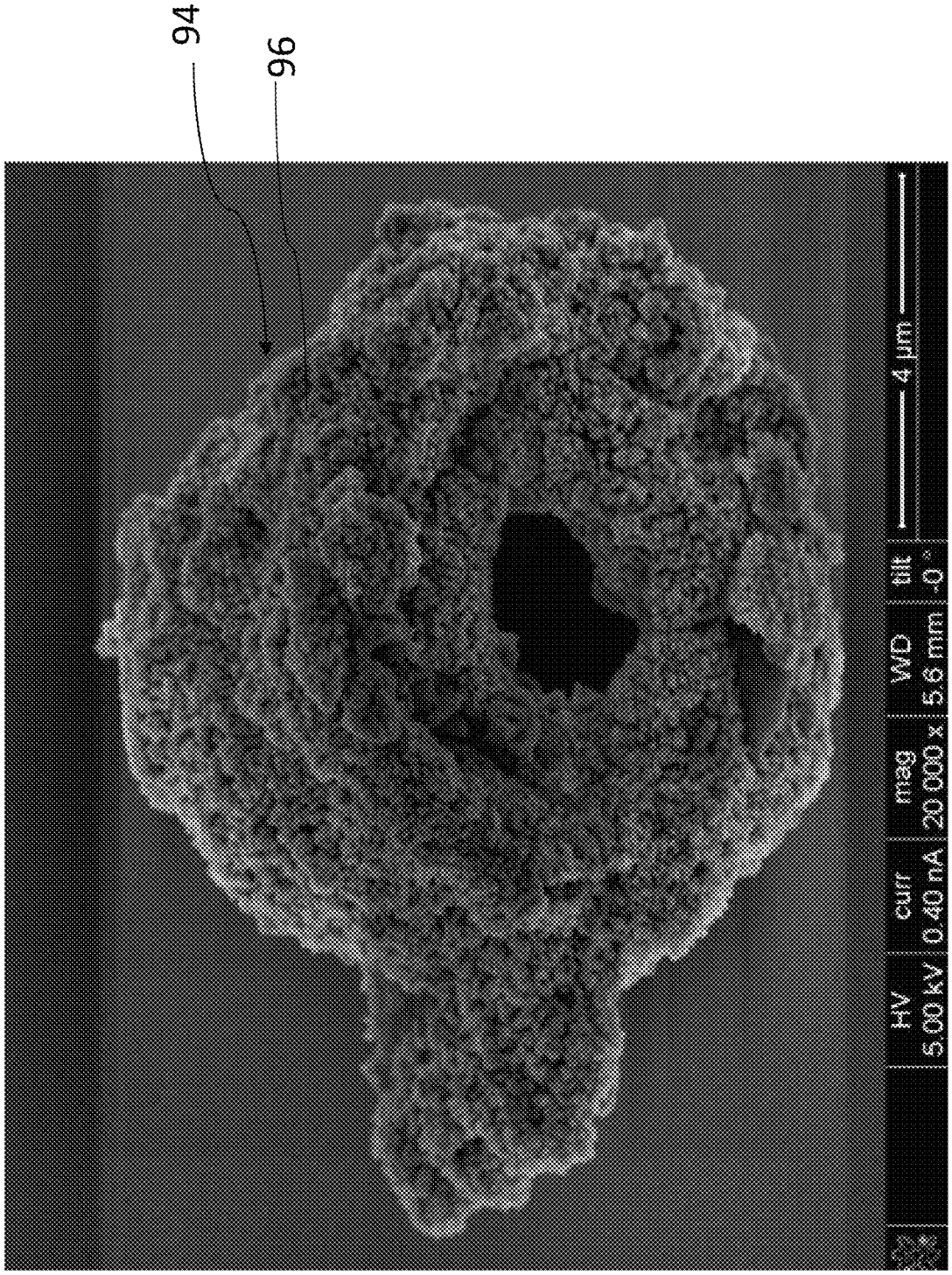


Fig. 5V

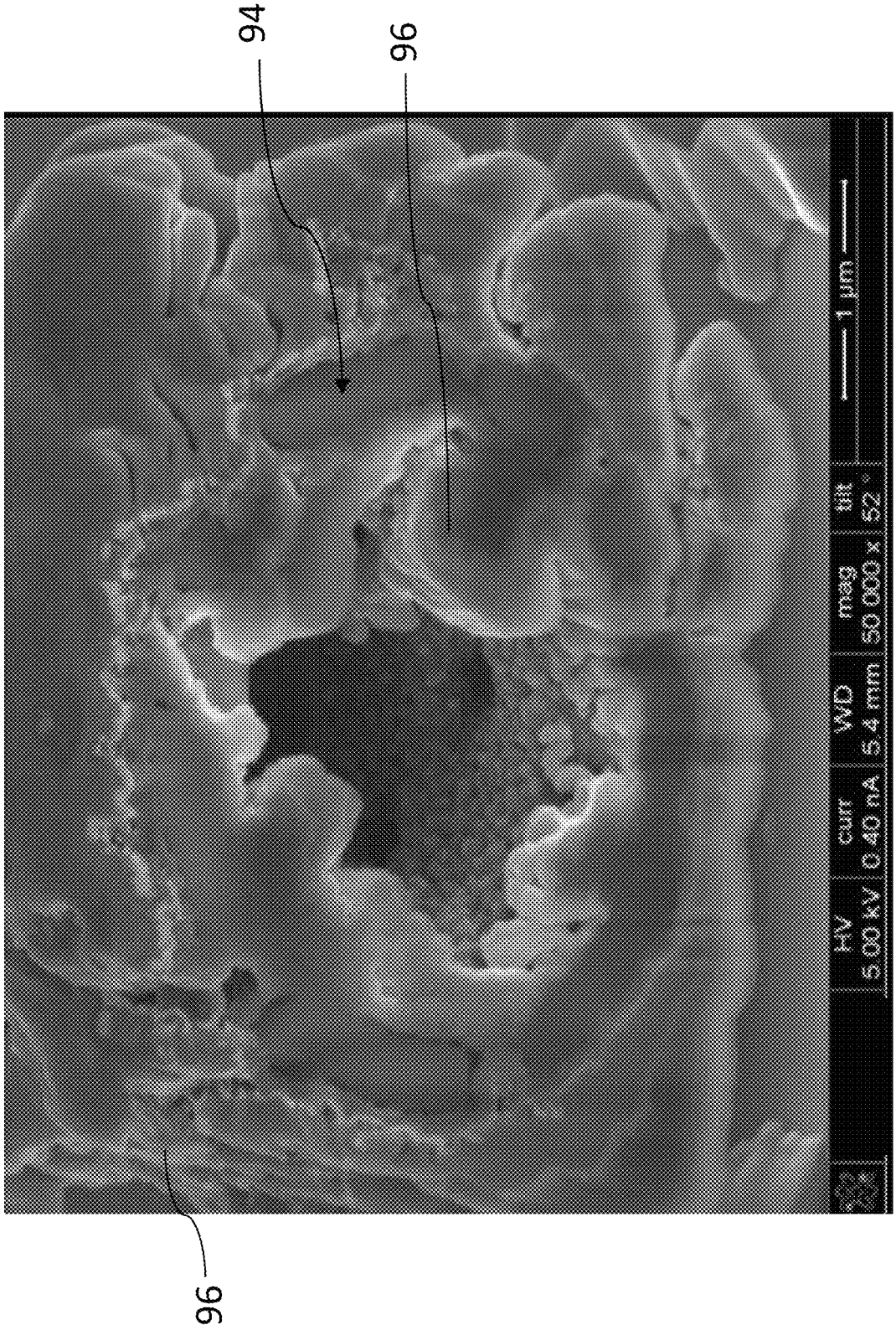


Fig. 5W

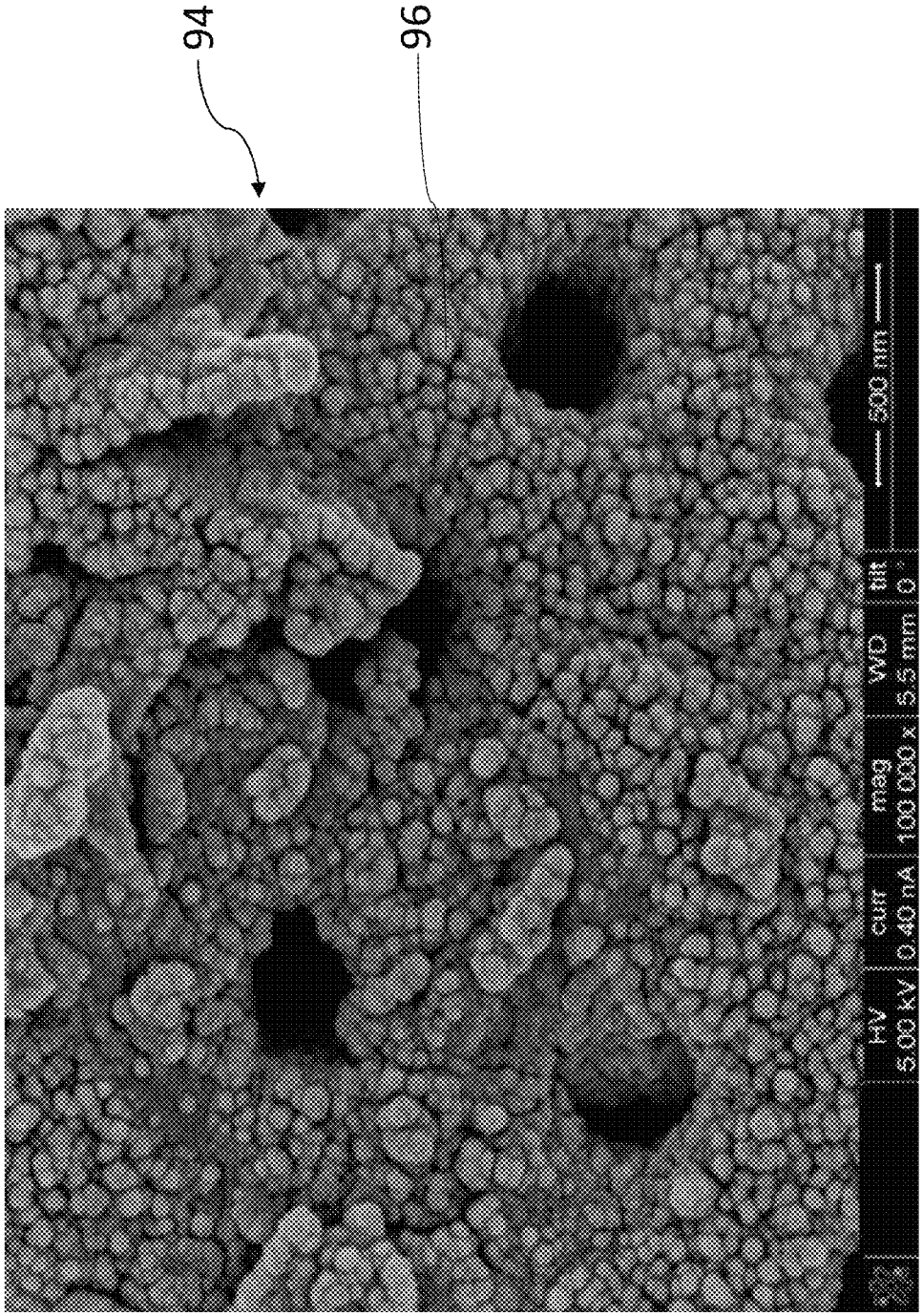


Fig. 5X

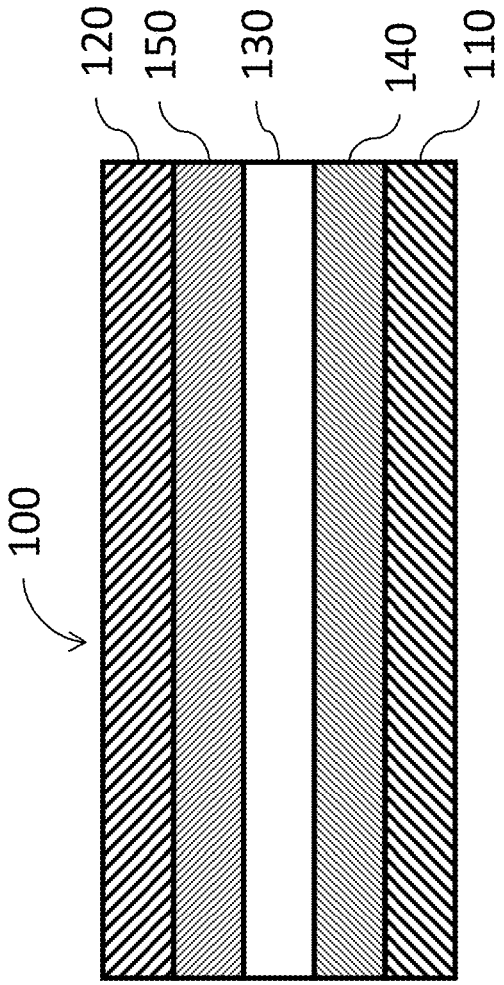


Fig. 6

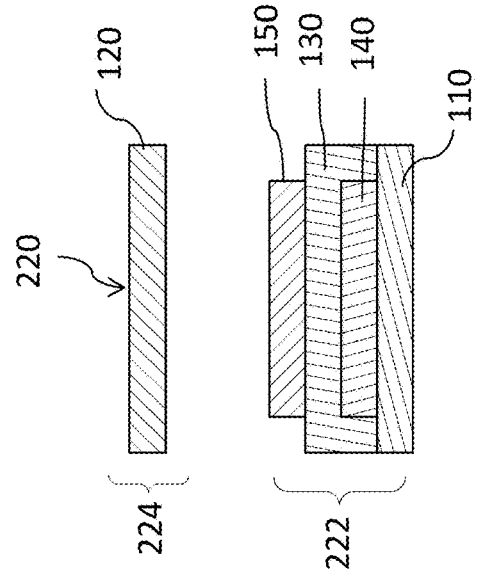


Fig. 7C

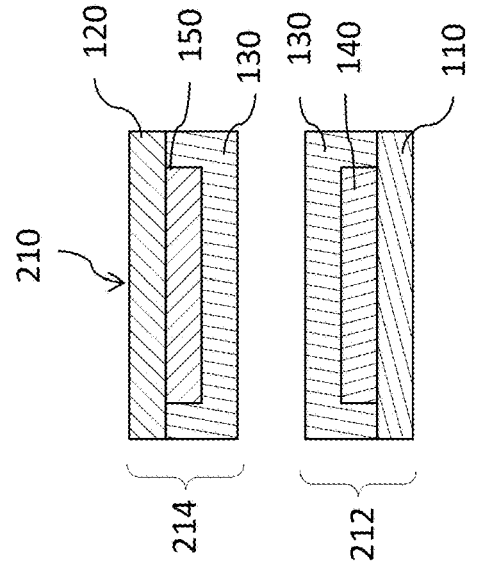


Fig. 7B

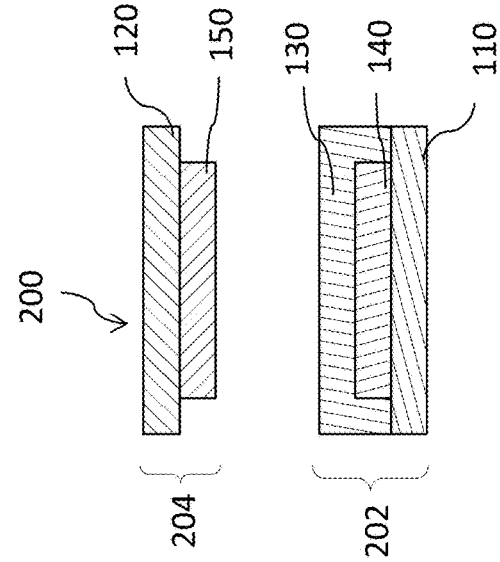


Fig. 7A

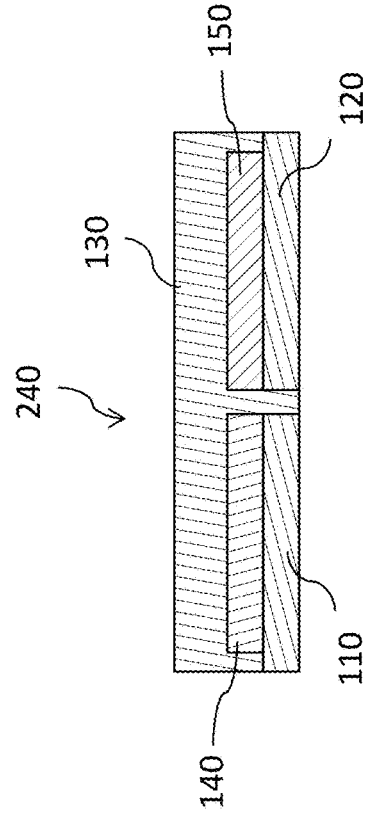


Fig. 7E

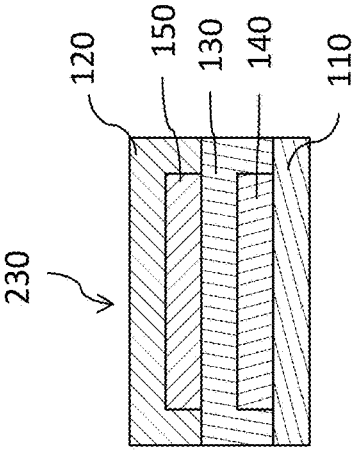


Fig. 7D

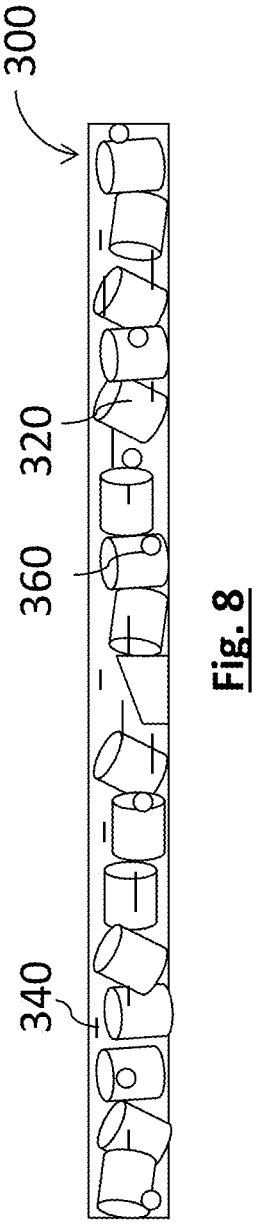


Fig. 8

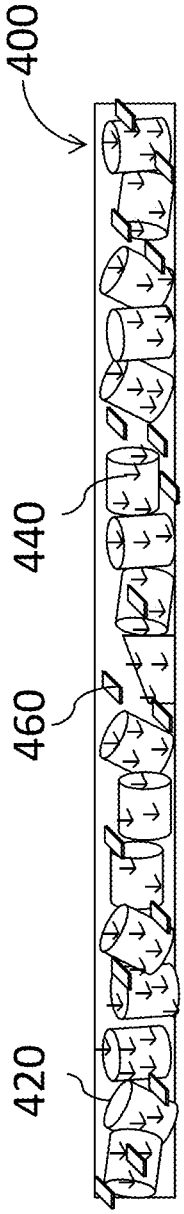


Fig. 9

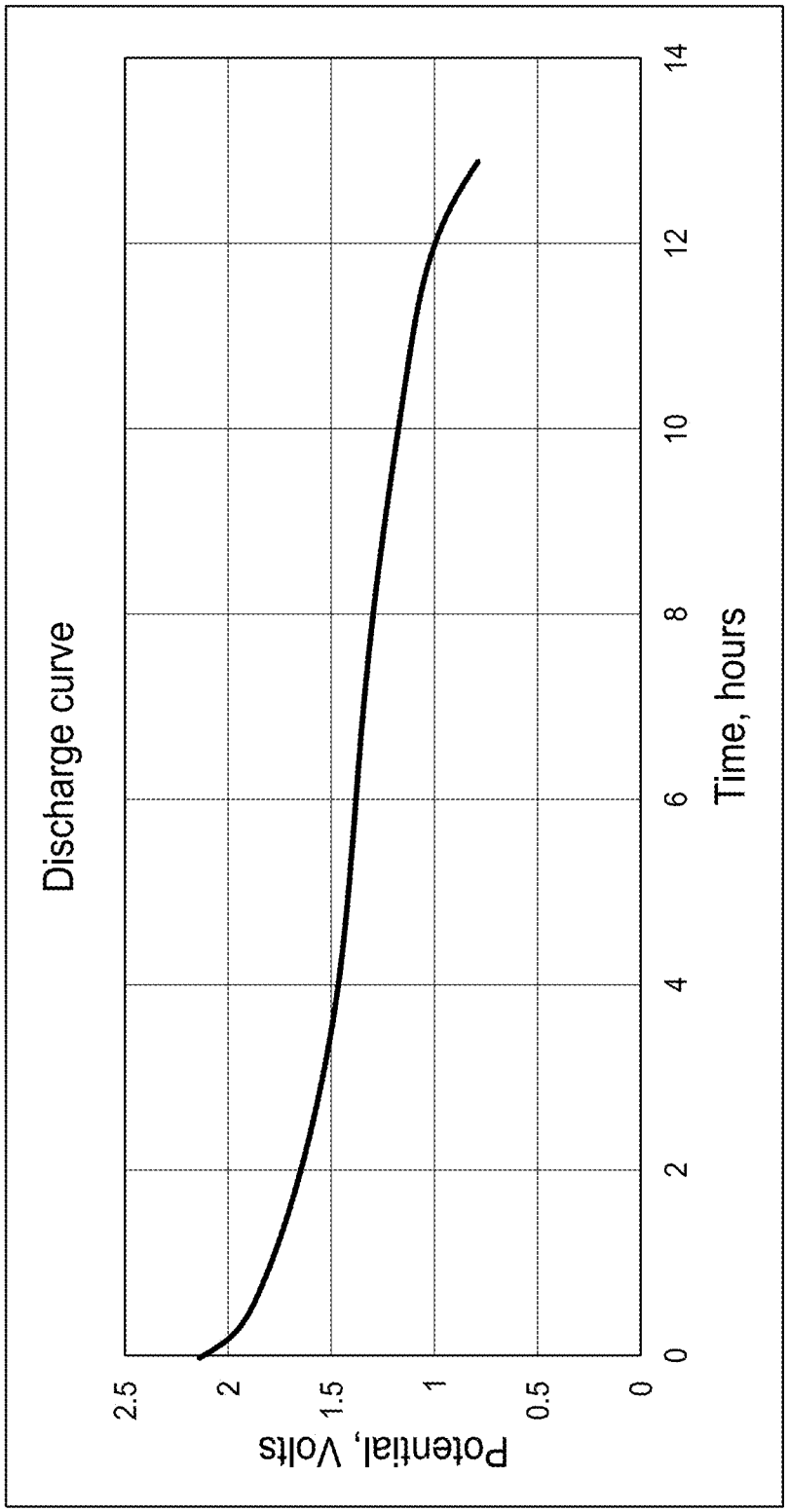

Discharge curve
Potential, Volts
2.5
2
1.5
1
0.5
0
Time, hours
0
2
4
6
8
10
12
14

Fig. 10

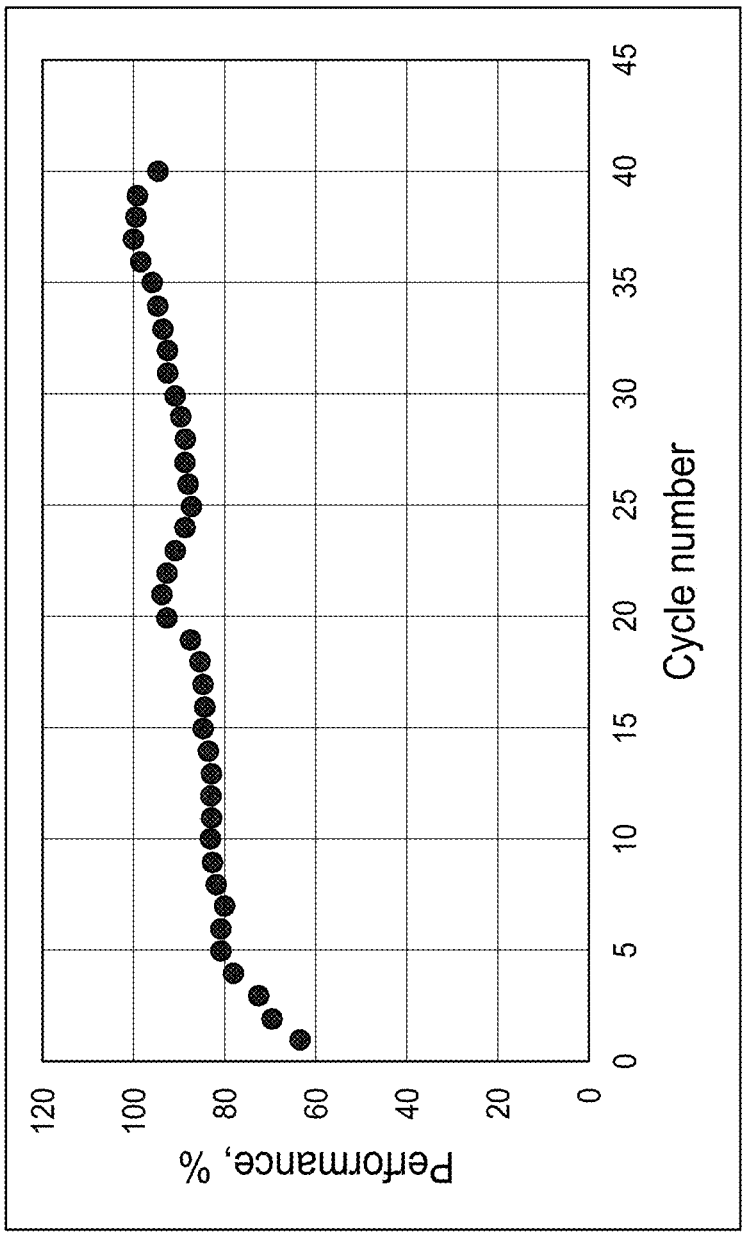

Performance, %
120
100
80
60
40
20
0
0
5
10
15
20
25
30
35
40
45
Cycle number

Fig. 11

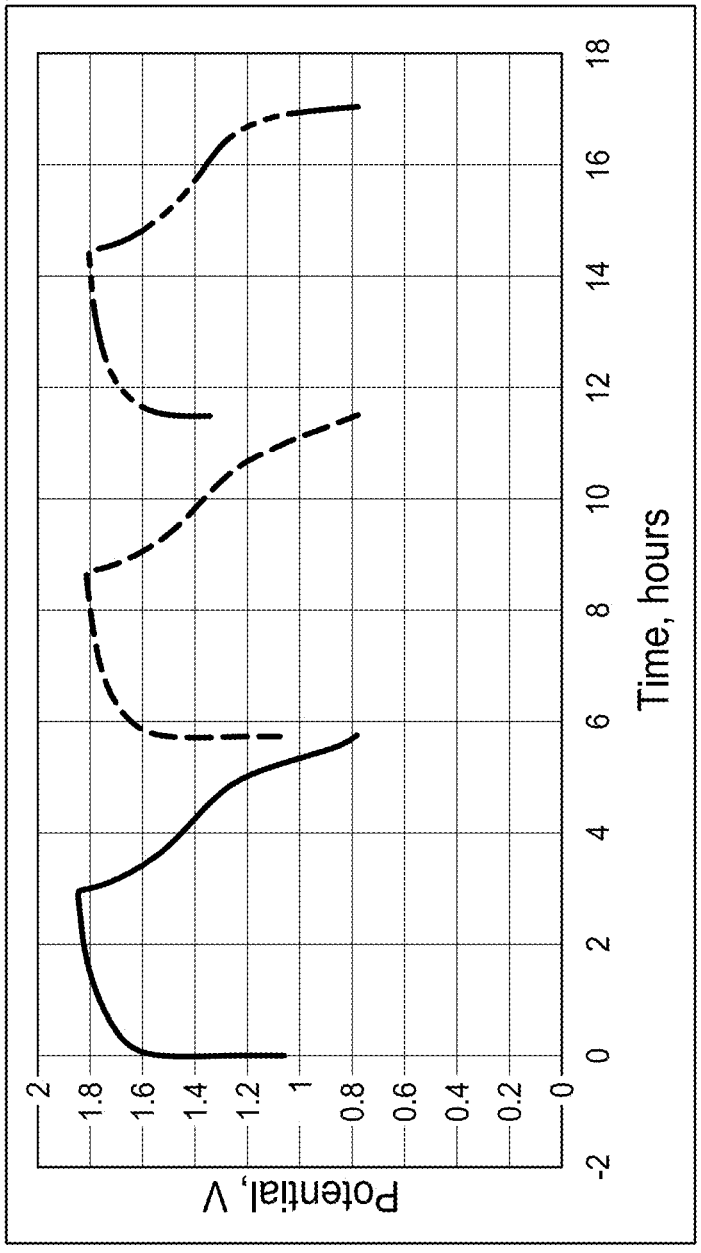

Potential, V
2
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
-2
0
2
4
6
8
10
12
14
16
18
Time, hours

Fig. 12

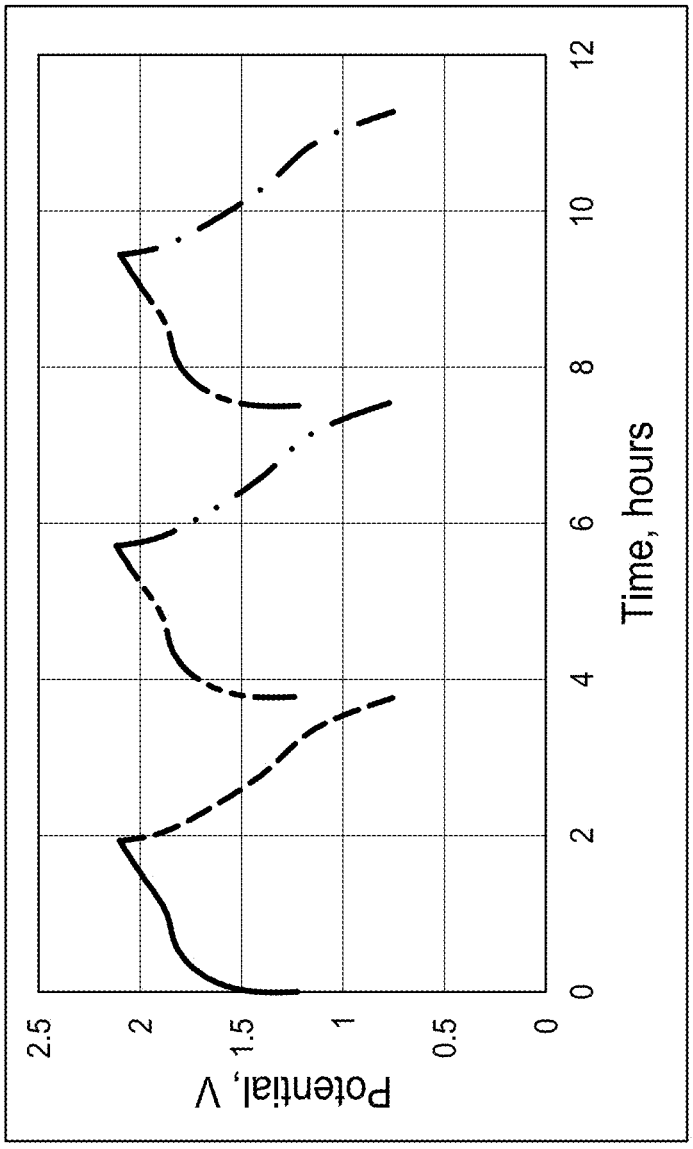


Fig. 13

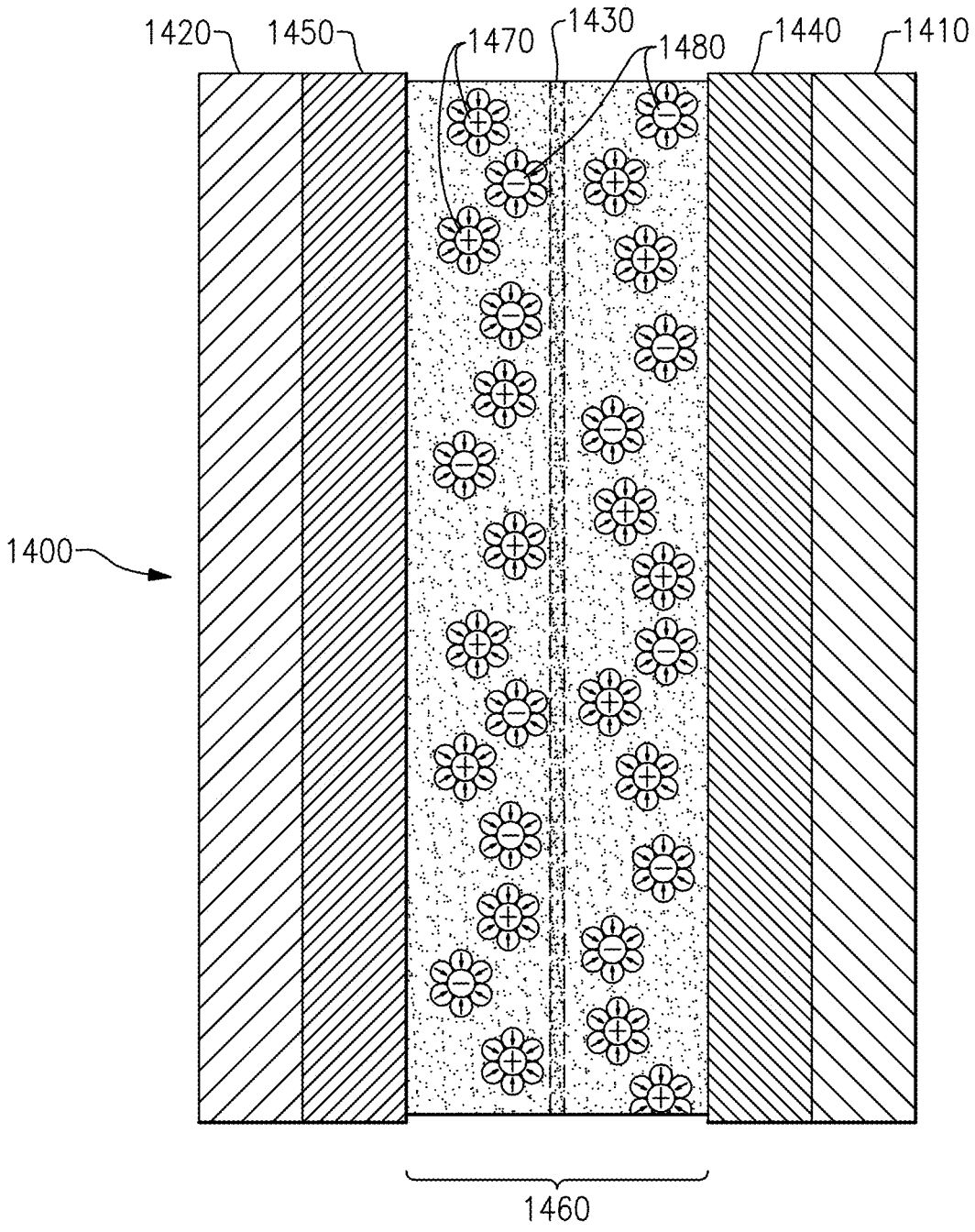


FIG.14A

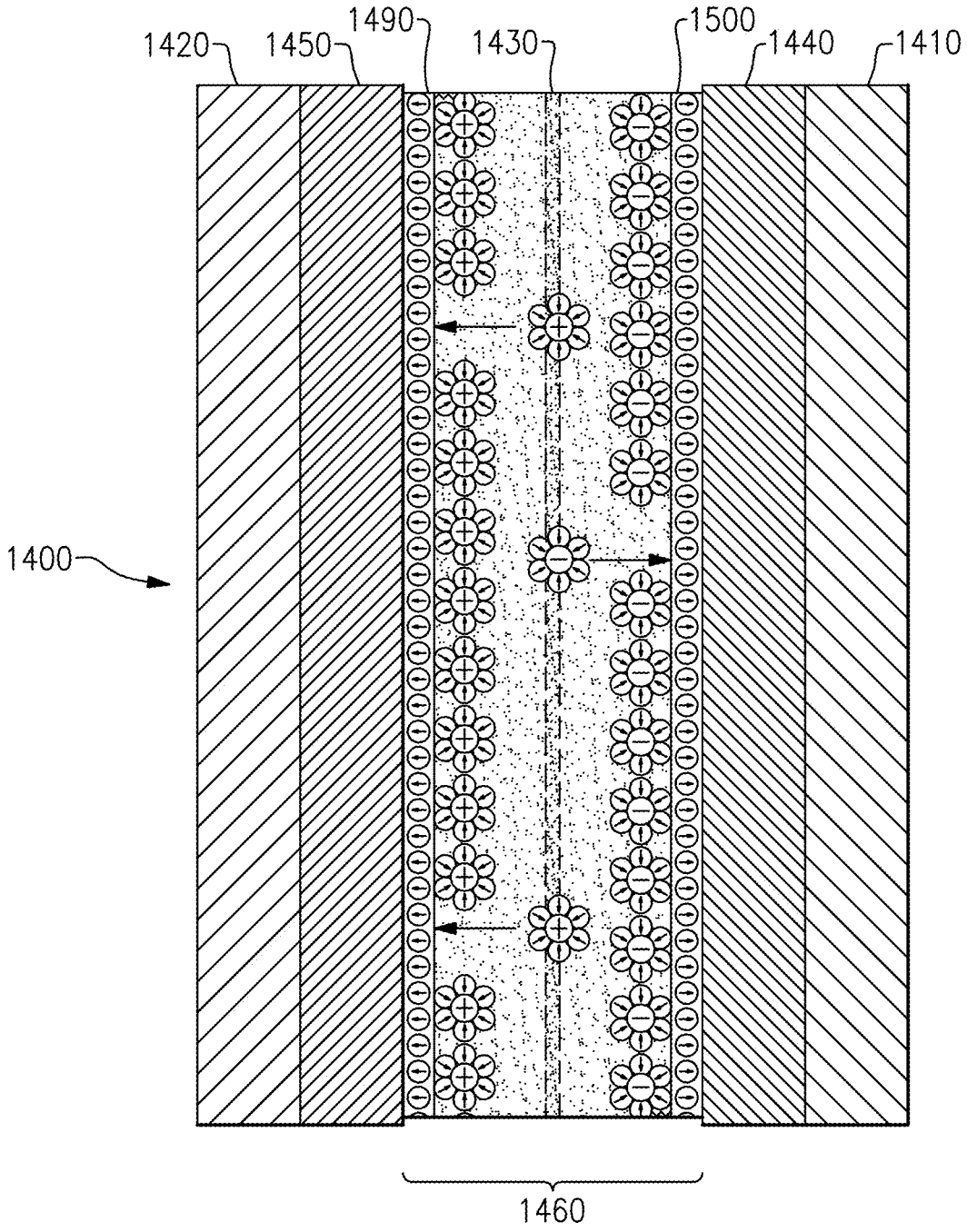


FIG.14B

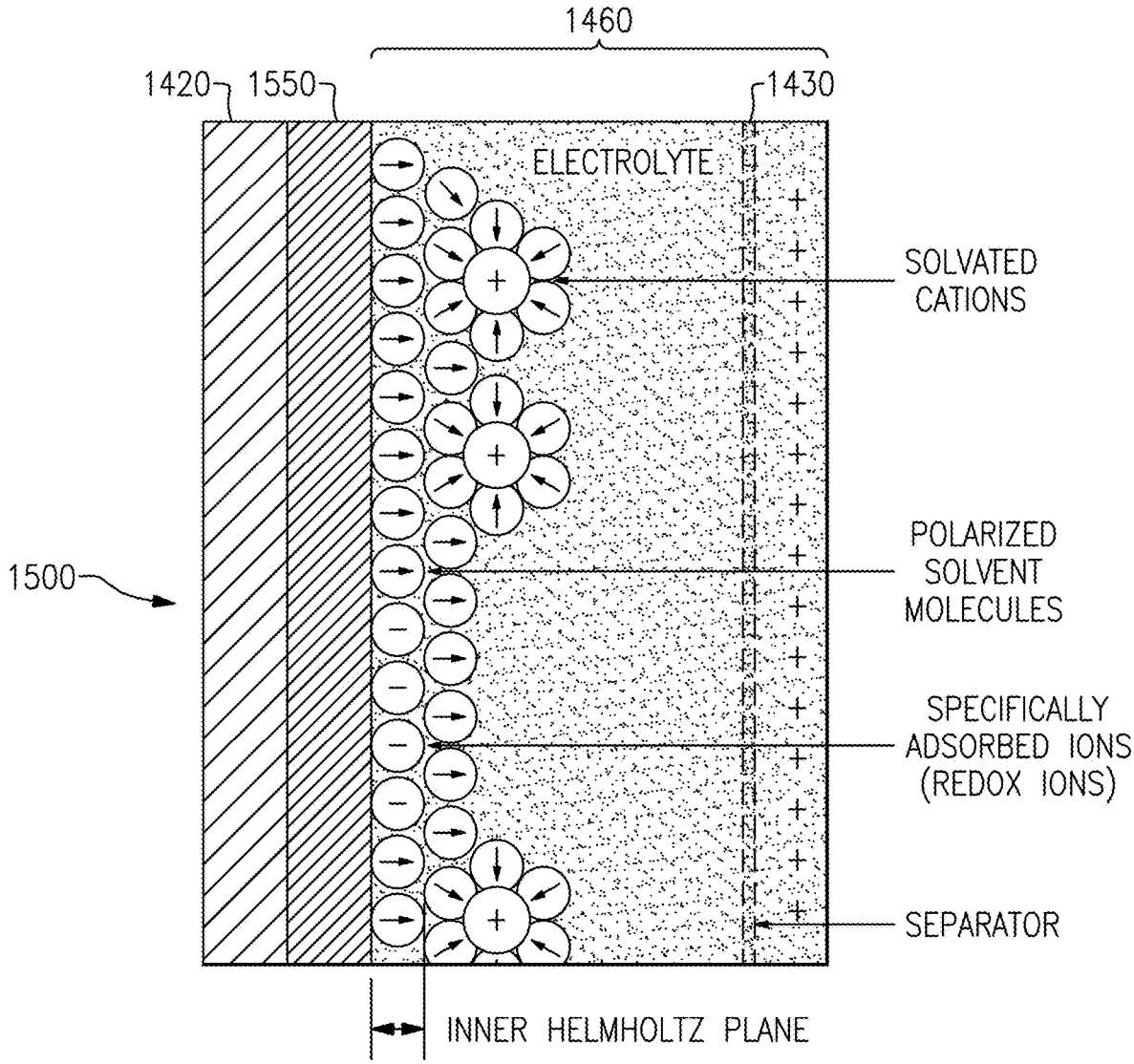

1460
1420
1550
1430
ELECTROLYTE
SOLVATED CATIONS
1500
POLARIZED SOLVENT MOLECULES
SPECIFICALLY ADSORBED IONS (REDOX IONS)
SEPARATOR
INNER HELMHOLTZ PLANE

FIG.15

FIG.16A

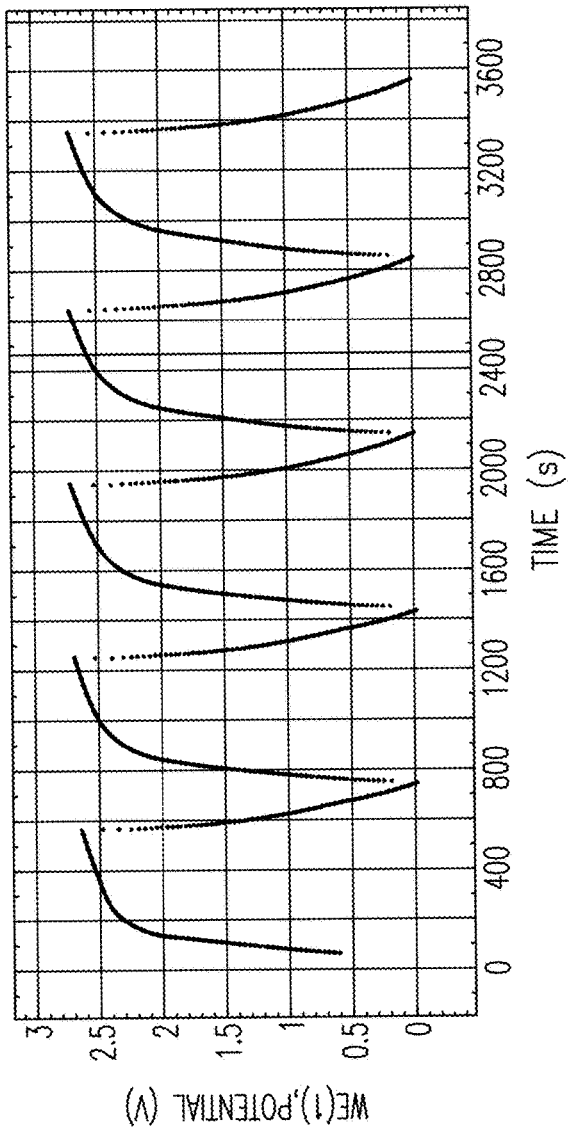


FIG.16B

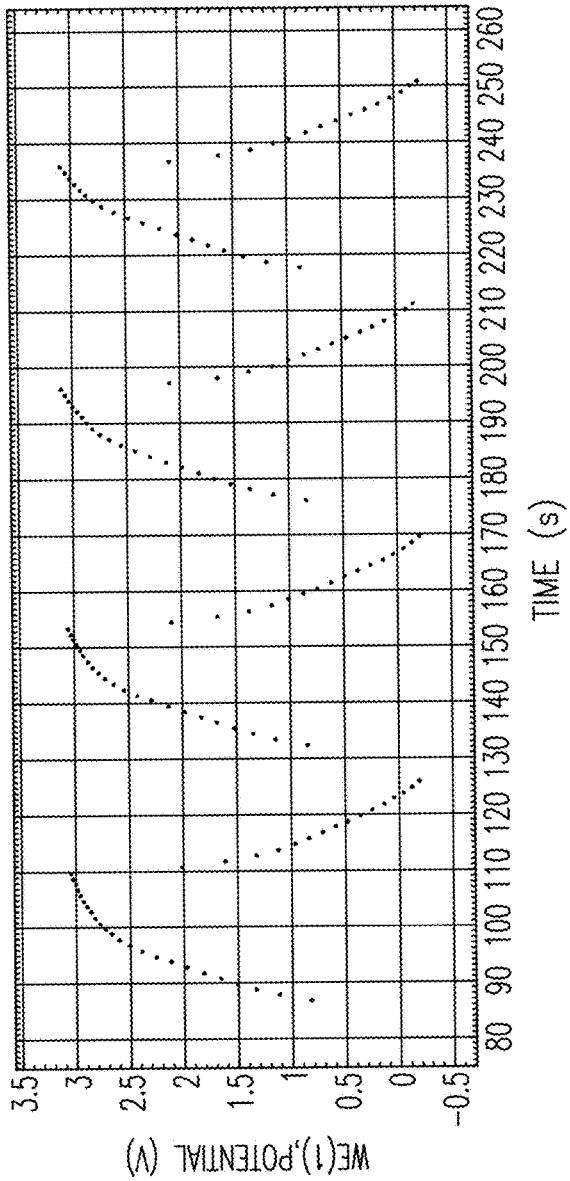


FIG.17A

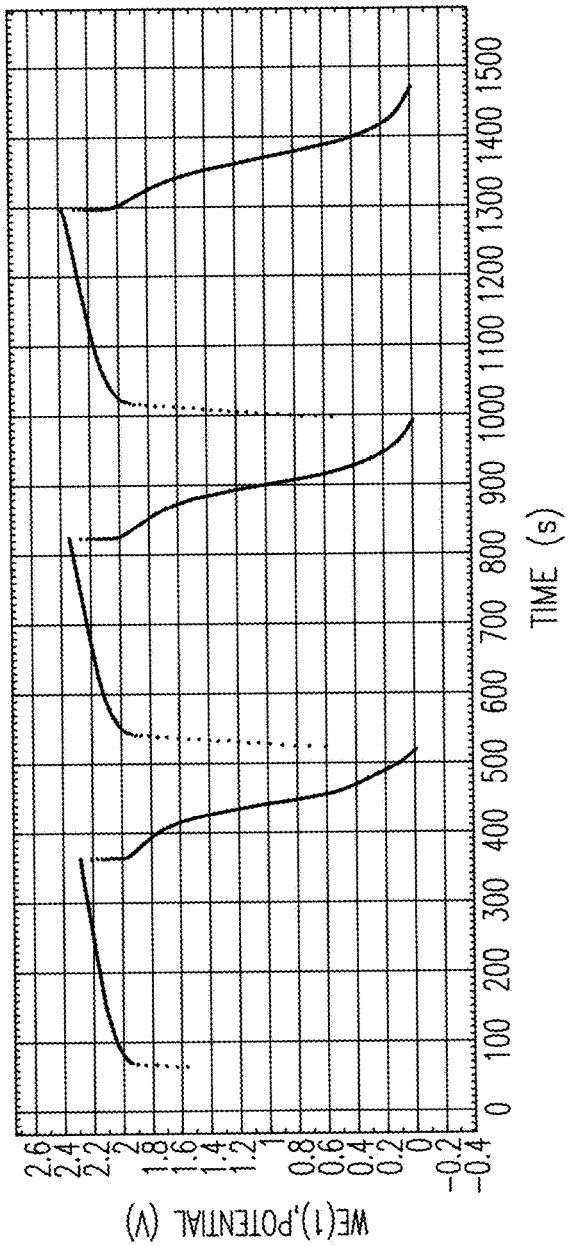


FIG.17B

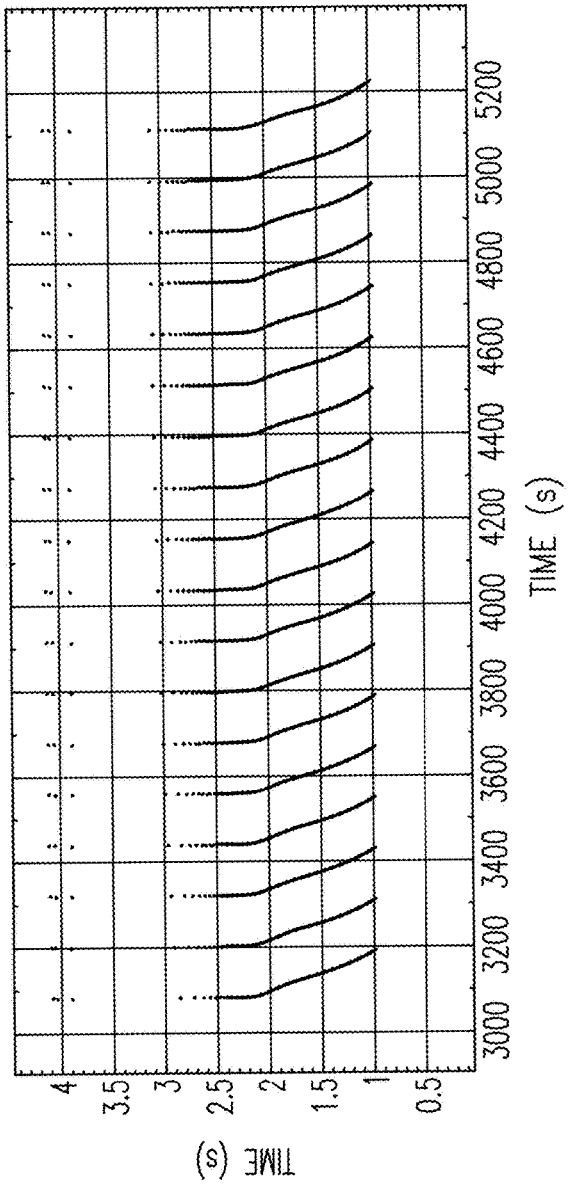


FIG.17C

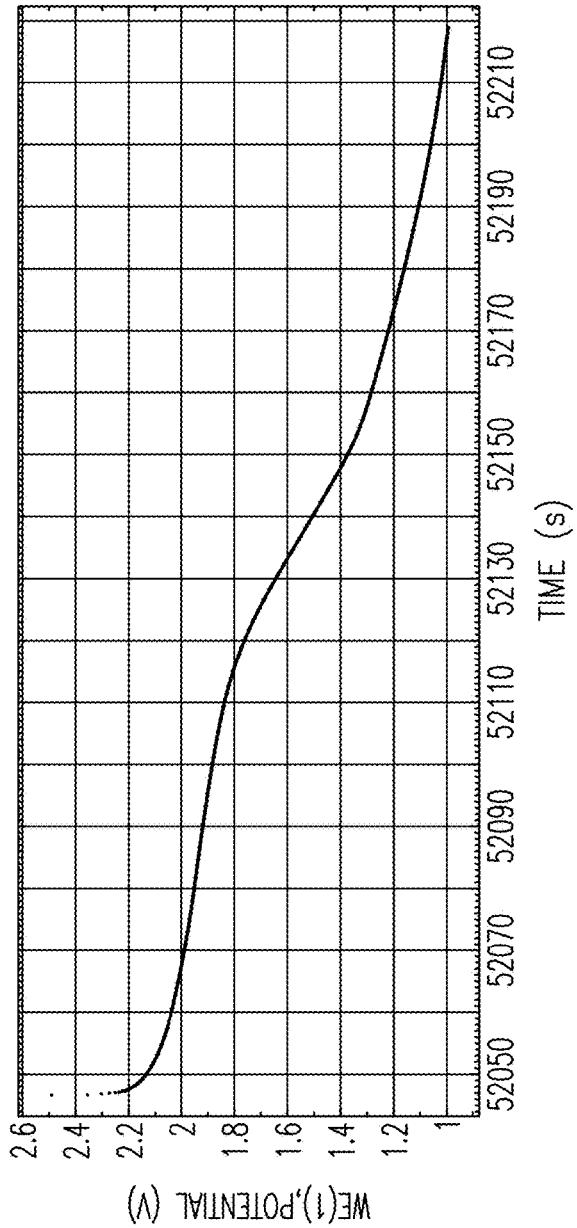


FIG.17D

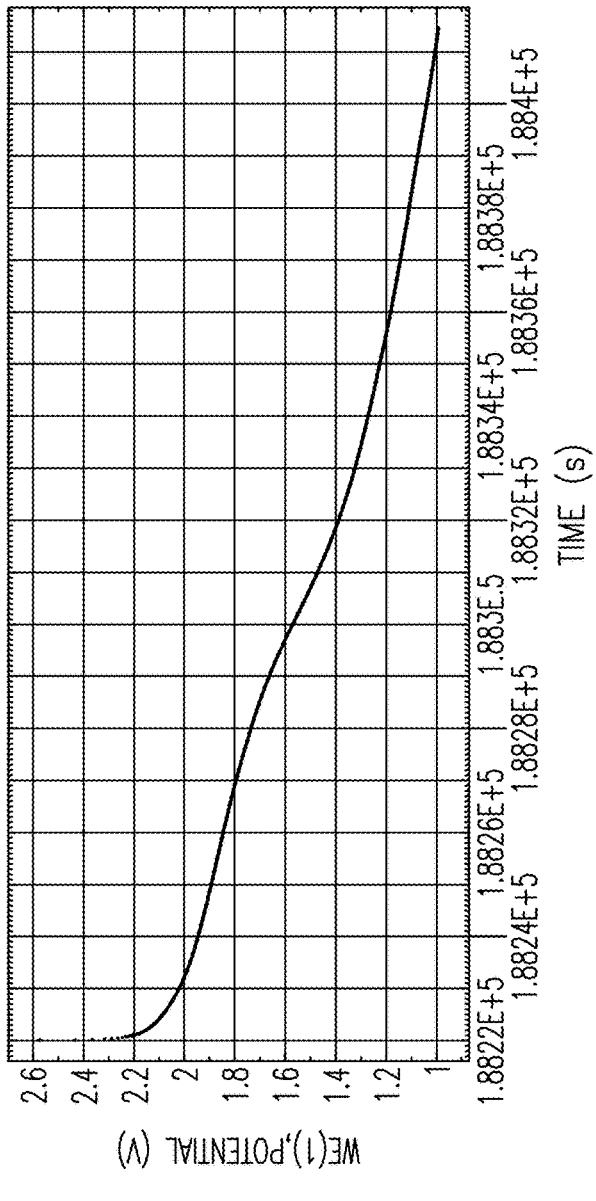


FIG.18A

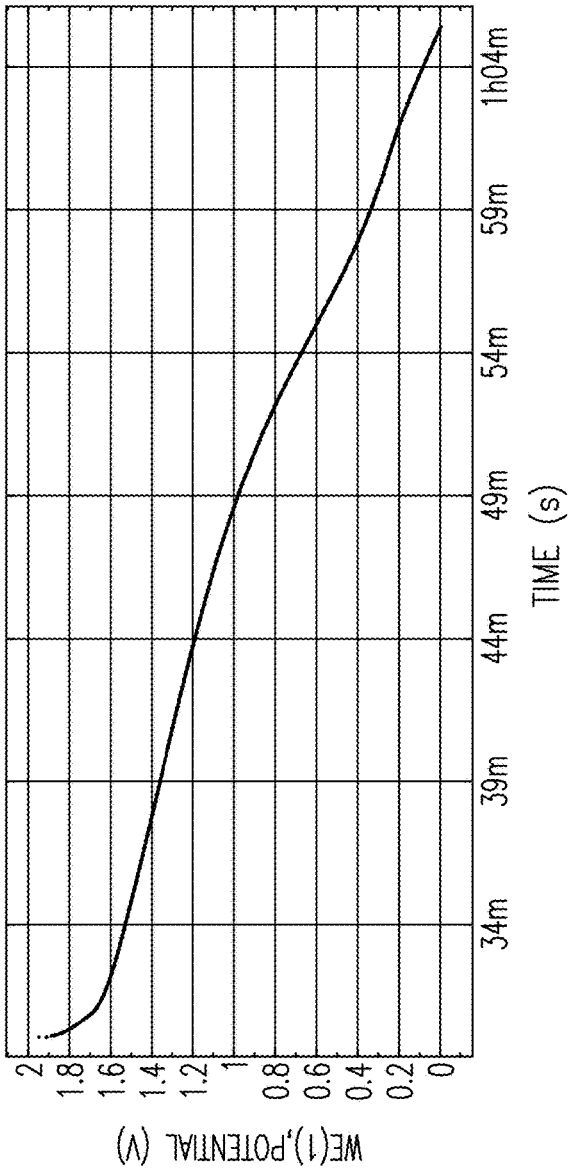


FIG.18B

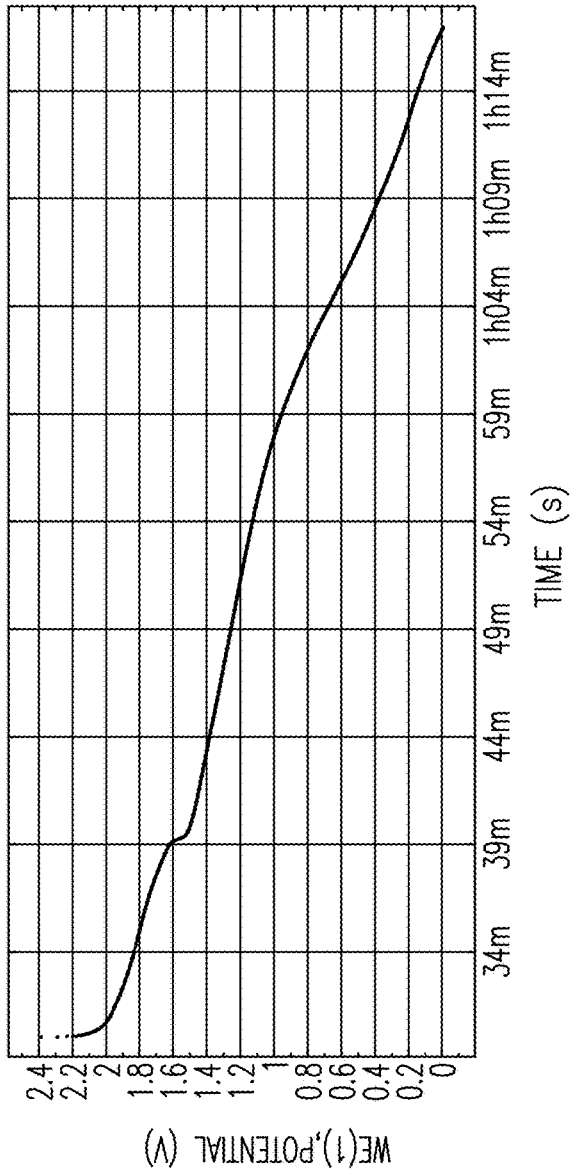


FIG.18C

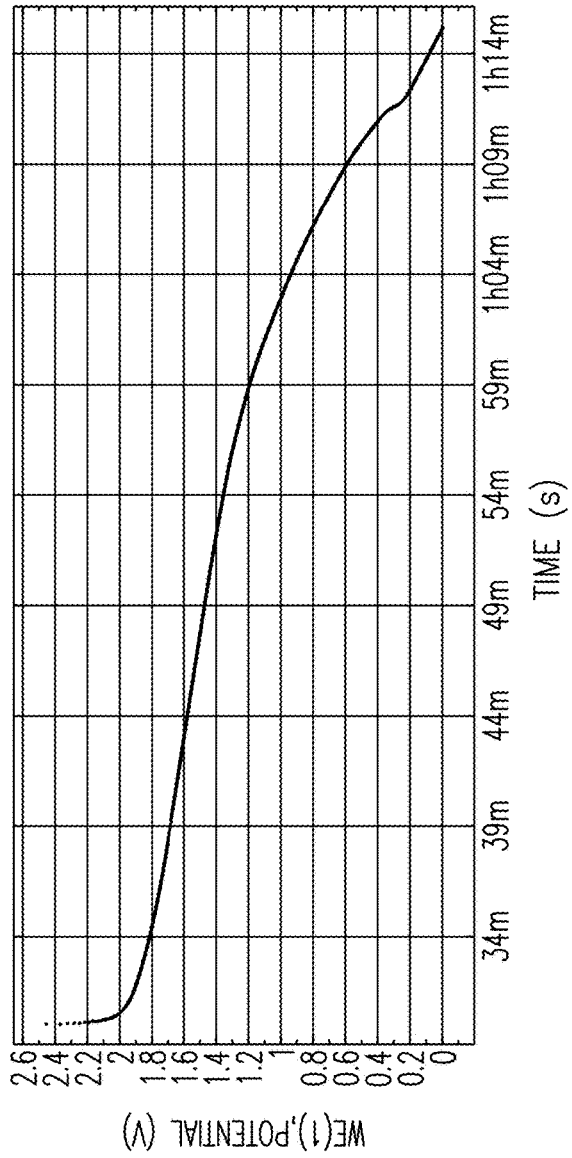
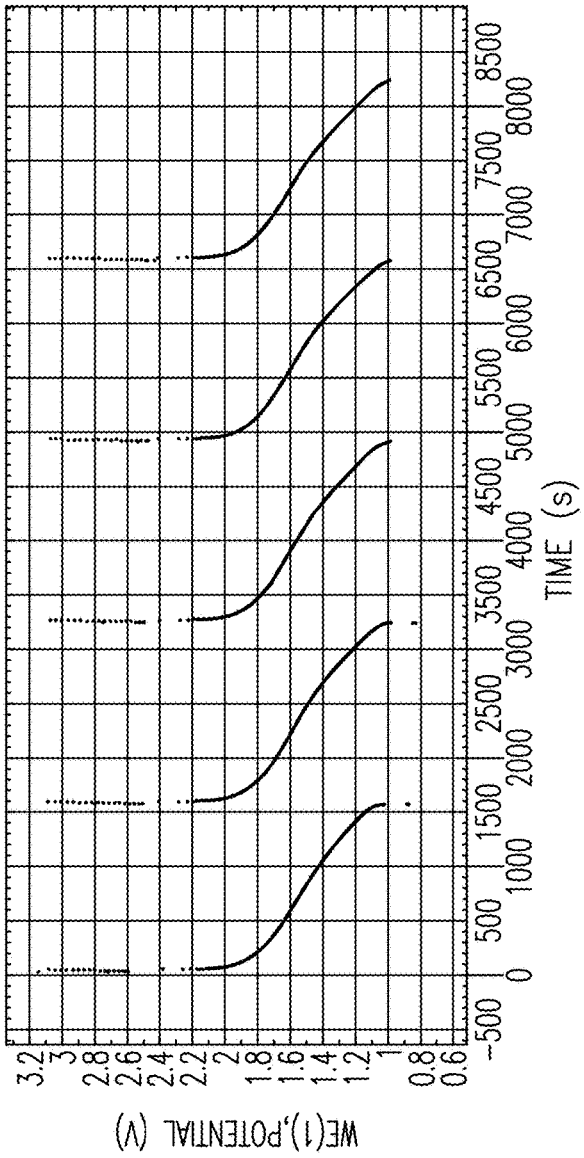


FIG.18D



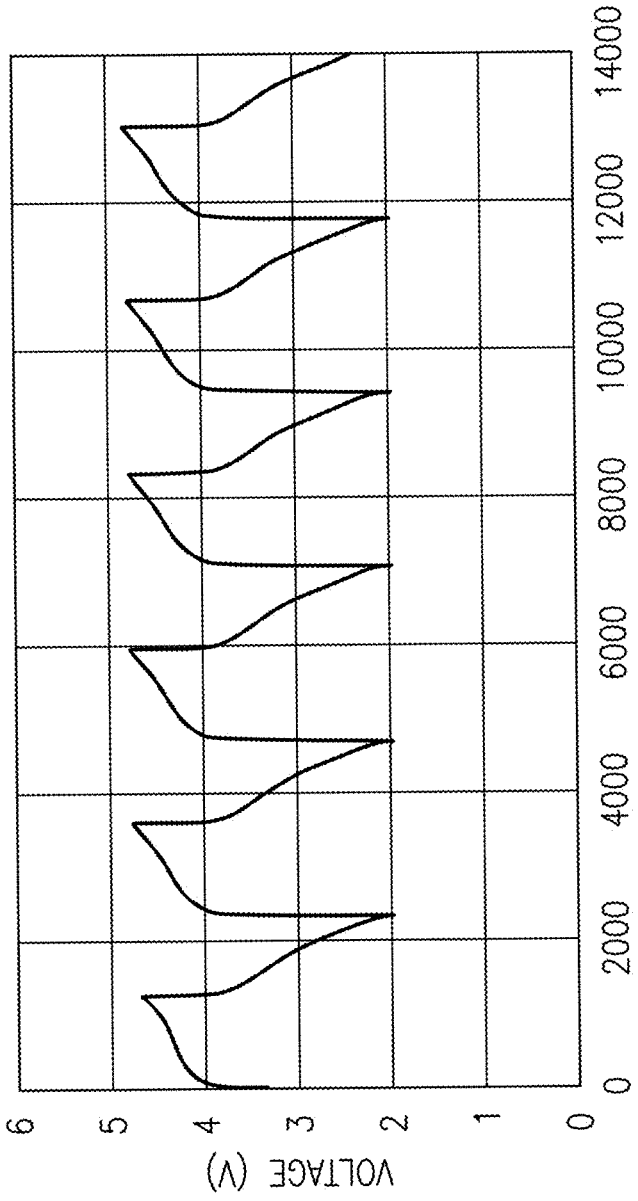

VOLTAGE (V)
0
1
2
3
4
5
6
0
2000
4000
6000
8000
10000
12000
14000
TIME (s)

FIG.18E

FIG.19A

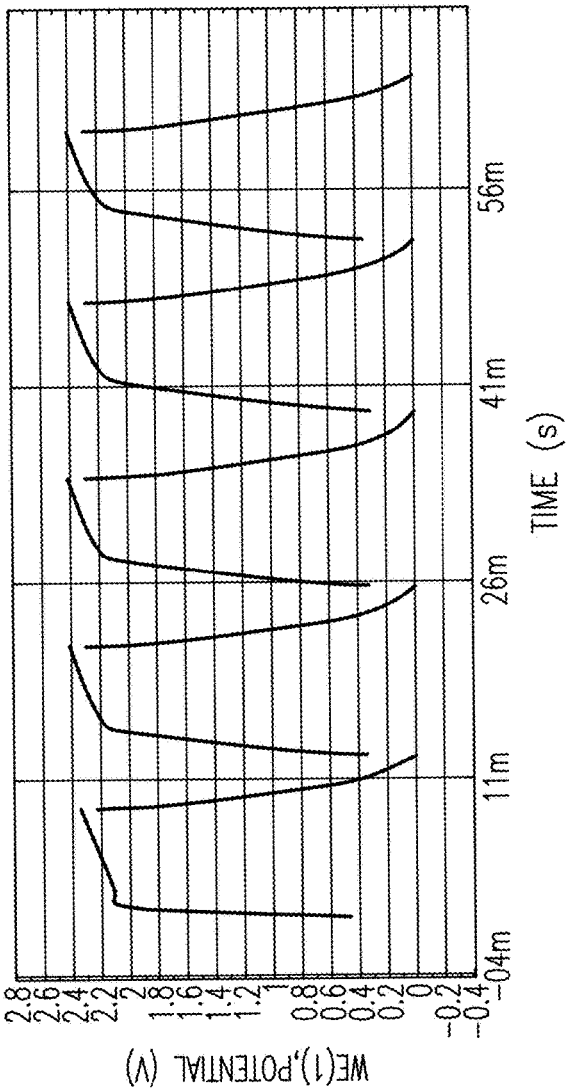
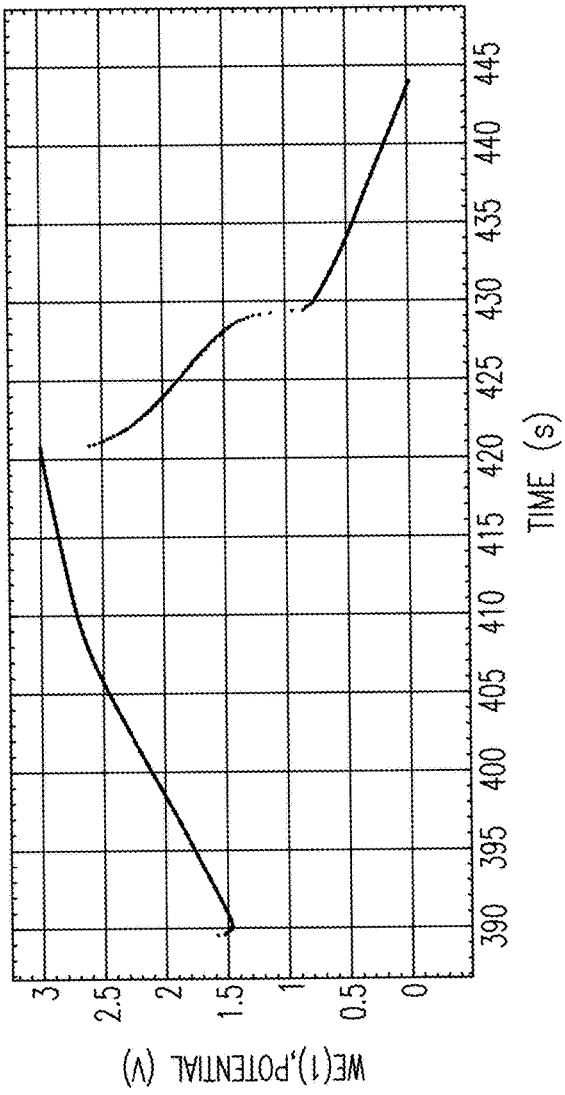


FIG.19B



DIATOMACEOUS ENERGY STORAGE DEVICES

CROSS REFERENCE TO RELATED APPLICATIONS

This application is a continuation of U.S. patent application Ser. No. 15/926,896, filed Mar. 20, 2018, entitled "Diatomaceous Energy Storage Devices," which is a continuation-in-part of U.S. patent application Ser. No. 15/808,757, filed Nov. 9, 2017, entitled "Diatomaceous Energy Storage Devices," which is a continuation of U.S. patent application Ser. No. 15/406,407, filed Jan. 13, 2017, entitled "Diatomaceous Energy Storage Devices," which is a continuation of U.S. patent application Ser. No. 14/745,709, filed Jun. 22, 2015, entitled "Diatomaceous Energy Storage Devices," which is continuation-in-part of U.S. patent application Ser. No. 14/161,658, filed Jan. 22, 2014, entitled "Diatomaceous Energy Storage Devices," which claims the benefit of U.S. Provisional Patent Application Ser. No. 61/862,469, filed Aug. 5, 2013, entitled "High Surface Area Nanoporous Energy Storage Devices," and which is a continuation-in-part of U.S. patent application Ser. No. 13/944,211, filed Jul. 17, 2013, entitled "Diatomaceous Energy Storage Devices," which claims the benefit of U.S. Provisional Patent Application Ser. No. 61/750,757, filed Jan. 9, 2013, entitled "Diatomaceous Energy Storage Devices," and U.S. Provisional Patent Application Ser. No. 61/673,149, filed Jul. 18, 2012, entitled "Diatomaceous Energy Storage Devices," each of which is incorporated herein by reference in its entirety.

BACKGROUND

Field

The present application relates to energy storage devices, and particularly to energy storage devices comprising frustules of diatoms.

Description of the Related Art

Diatoms typically include unicellular eukaryotes, such as single-celled algae. Diatoms are abundant in nature and can be found in both fresh water and marine environments. Generally, diatoms are enclosed by a frustule having two valves fitted together through a connective zone comprising girdle elements. Diatomaceous earth, sometimes known as diatomite, can be a source of frustules. Diatomaceous earth comprises fossilized frustules and can be used in a diverse range of applications, including as a filtering agent, a filling agent for paints or plastics, an adsorbent, cat litter, or an abrasive material.

Frustules often comprise a significant amount of silica (SiO_2), along with alumina, iron oxide, titanium oxide, phosphate, lime, sodium, and/or potassium. Frustules are typically electrically insulating. Frustules may comprise a wide variety of dimensions, surface features, shapes, and other attributes. For example, frustules may comprise diverse shapes, including but not limited to cylinders, spheres, discs, or prisms. Frustules comprise a symmetrical shape or a non-symmetrical shape. Diatoms may be categorized according to the shape and/or symmetry of the frustules, for example grouping the diatoms based on existence or lack of radial symmetry. Frustules may comprise dimensions within a range from less than about one micron to about hundreds of microns. Frustules may also comprise

varying porosity, having numerous pores or slits. Pores or slits of frustules may vary in shape, size, and/or density. For example, frustules may comprise pores having dimensions from about 5 nm to about 1000 nm.

Frustules may comprise significant mechanical strength or resistance to shear stress, for example due to the dimensions of the frustule, frustule shape, porosity, and/or material composition.

SUMMARY

An energy storage device such as a battery (e.g., rechargeable battery), fuel cell, capacitor, and/or supercapacitor (e.g., electric double-layer capacitor (EDLC), pseudo capacitor, symmetric capacitor), may be fabricated using frustules embedded in at least one layer of the energy storage device. The frustules can be sorted to have a selected shape, dimension, porosity, material, surface feature, and/or another suitable frustule attribute, which may be uniform or substantially uniform or which may vary. The frustules may include a frustule surface modifying structure and/or material. The energy storage device may include layers such as electrodes, separators, and/or current collectors. For example, a separator may be positioned between a first electrode and a second electrode, a first current collector may be coupled to the first electrode, and a second current collector may be coupled to the second electrode. At least one of the separator, the first electrode, and the second electrode may include the frustules. Inclusion of frustules in at least a portion of an energy storage device can help to fabricate the energy storage device using printing technology, including screen printing, roll-to-roll printing, ink-jet printing, and/or another suitable printing process. The frustules can provide structural support for an energy storage device layer and help the energy storage device layer to maintain a uniform or substantially uniform thickness during manufacturing and/or use. Porous frustules can allow unimpeded or substantially unimpeded flow of electrons or ionic species. Frustules including surface structures or material can increase conductivity of a layer.

In some embodiments, a printed energy storage device comprises a first electrode, a second electrode, and a separator between the first electrode and the second electrode. At least one of the first electrode, the second electrode, and the separator includes frustules.

In some embodiments, the separator includes the frustules. In some embodiments, the first electrode includes the frustules. In some embodiments, the separator and the first electrode include the frustules. In some embodiments, the second electrode includes the frustules. In some embodiments, the separator and the second electrode include the frustules. In some embodiments, the first electrode and the second electrode include the frustules. In some embodiments, the separator, the first electrode, and the second electrode include the frustules.

In some embodiments, the frustules have a substantially uniform property. In some embodiments, the property comprises shape, for example including a cylinder, a sphere, a disc, or a prism. In some embodiments, the property comprises a dimension, for example including diameter, length, or a longest axis. In some embodiments, the property comprises porosity. In some embodiments, the property comprises mechanical strength.

In some embodiments, the frustules comprise a surface modifying structure. In some embodiments, the surface modifying structure includes a conductive material. In some embodiments, the conductive material includes at least one

of silver, aluminum, tantalum, copper, lithium, magnesium, and brass. In some embodiments, the surface modifying structure includes zinc oxide (ZnO). In some embodiments, the surface modifying structure comprises a semiconductor. In some embodiments, the semiconductor includes at least one of silicon, germanium, silicon germanium, and gallium arsenide. In some embodiments, the surface modifying structure comprises at least one of a nanowire, a nanoparticle, and a structure having a rosette shape. In some embodiments, the surface modifying structure is on an exterior surface of the frustules. In some embodiments, the surface modifying structure is on an interior surface of the frustules. In some embodiments, the surface modifying structure is on an interior surface and an exterior surface of the frustules.

In some embodiments, the frustules comprise a surface modifying material. In some embodiments, the surface modifying material comprises a conductive material. In some embodiments, the surface modifying material includes at least one of silver, aluminum, tantalum, copper, lithium, magnesium, and brass. In some embodiments, the surface modifying material includes ZnO. In some embodiments, the surface modifying material includes a semiconductor. In some embodiments, the semiconductor includes at least one of silicon, germanium, silicon germanium, and gallium arsenide. In some embodiments, the surface modifying material is on an exterior surface of the frustules. In some embodiments, the surface modifying material is on an interior surface of the frustules. In some embodiments, the surface modifying material is on an exterior surface and an interior surface of the frustules.

In some embodiments, the first electrode comprises a conductive filler. In some embodiments, the second electrode comprises a conductive filler. In some embodiments, the first electrode and the second electrode comprise a conductive filler. In some embodiments, the conductive filler comprises graphitic carbon. In some embodiments, the conductive filler comprises graphene. In some embodiments, the conductive filler comprises carbon nanotubes.

In some embodiments, the first electrode comprises an adherence material. In some embodiments, the second electrode comprises an adherence material. In some embodiments, the first electrode and the second electrode comprise an adherence material. In some embodiments, the separator comprises an adherence material. In some embodiments, the first electrode and the separator comprise an adherence material. In some embodiments, the second electrode and the separator comprise an adherence material. In some embodiments, the first electrode, the second electrode, and the separator comprise an adherence material. In some embodiments, the adherence material comprises a polymer.

In some embodiments, the separator comprises an electrolyte. In some embodiments, the electrolyte comprises at least one of an ionic liquid, an acid, a base, and a salt. In some embodiments, the electrolyte comprises an electrolytic gel.

In some embodiments, the device comprises a first current collector in electrical communication with the first electrode. In some embodiments, the device comprises a second current collector in electrical communication with the second electrode. In some embodiments, the device comprises a first current collector in electrical communication with the first electrode and a second current collector in electrical communication with the second electrode.

In some embodiments, the printed energy storage device comprises a capacitor. In some embodiments, the printed energy storage device comprises a supercapacitor. In some embodiments, the printed energy storage device comprises a battery.

In some embodiments, a system comprises a plurality of the printed energy storage devices as described herein stacked on top of each other. In some embodiments, an electrical device comprises the printed energy storage devices described herein or the system.

In some embodiments, a membrane for a printed energy storage device comprises frustules.

In some embodiments, the frustules have a substantially uniform property. In some embodiments, the property comprises shape, for example including a cylinder, a sphere, a disc, or a prism. In some embodiments, the property comprises a dimension, for example including diameter, length, or a longest axis. In some embodiments, the property comprises porosity. In some embodiments, the property comprises mechanical strength.

In some embodiments, the frustules comprise a surface modifying structure. In some embodiments, the surface modifying structure includes a conductive material. In some embodiments, the conductive material includes at least one of silver, aluminum, tantalum, copper, lithium, magnesium, and brass. In some embodiments, the surface modifying structure includes zinc oxide (ZnO). In some embodiments, the surface modifying structure comprises a semiconductor. In some embodiments, the semiconductor includes at least one of silicon, germanium, silicon germanium, and gallium arsenide. In some embodiments, the surface modifying structure comprises at least one of a nanowire, a nanoparticle, and a structure having a rosette shape. In some embodiments, the surface modifying structure is on an exterior surface of the frustules. In some embodiments, the surface modifying structure is on an interior surface of the frustules. In some embodiments, the surface modifying structure is on an interior surface and an exterior surface of the frustules.

In some embodiments, the frustules comprise a surface modifying material. In some embodiments, the surface modifying material comprises a conductive material. In some embodiments, the surface modifying material includes at least one of silver, aluminum, tantalum, copper, lithium, magnesium, and brass. In some embodiments, the surface modifying material includes ZnO. In some embodiments, the surface modifying material includes a semiconductor. In some embodiments, the semiconductor includes at least one of silicon, germanium, silicon germanium, and gallium arsenide. In some embodiments, the surface modifying material is on an exterior surface of the frustules. In some embodiments, the surface modifying material is on an interior surface of the frustules. In some embodiments, the surface modifying material is on an exterior surface and an interior surface of the frustules.

In some embodiments, the membrane further comprises a conductive filler. In some embodiments, the conductive filler comprises graphitic carbon. In some embodiments, the conductive filler comprises graphene.

In some embodiments, the membrane further comprises an adherence material. In some embodiments, the adherence material comprises a polymer.

In some embodiments, the membrane further comprises an electrolyte. In some embodiments, the electrolyte comprises at least one of an ionic liquid, an acid, a base, and a salt. In some embodiments, the electrolyte comprises an electrolytic gel.

In some embodiments, an energy storage device comprises the membrane as described herein. In some embodi-

ments, the printed energy storage device comprises a capacitor. In some embodiments, the printed energy storage device comprises a supercapacitor. In some embodiments, the printed energy storage device comprises a battery. In some embodiments, a system comprises a plurality of energy storage devices as described herein stacked on top of each other. In some embodiments, an electrical device comprises the printed energy storage devices described herein or the system.

In some embodiments, a method of manufacturing a printed energy storage device comprises forming a first electrode, forming a second electrode, and forming a separator between the first electrode and the second electrode. At least one of the first electrode, the second electrode, and the separator includes frustules.

In some embodiments, the separator includes the frustules. In some embodiments, forming the separator includes forming a dispersion of the frustules. In some embodiments, forming the separator includes screen printing the separator. In some embodiments, forming the separator includes forming a membrane of the frustules. In some embodiments, forming the separator includes roll-to-roll printing the membrane including the separator.

In some embodiments, the first electrode includes the frustules. In some embodiments, forming the first electrode includes forming a dispersion of the frustules. In some embodiments, forming the first electrode includes screen printing the first electrode. In some embodiments, forming the first electrode includes forming a membrane of the frustules. In some embodiments, forming the first electrode includes roll-to-roll printing the membrane including the first electrode.

In some embodiments, the second electrode includes the frustules. In some embodiments, forming the second electrode includes forming a dispersion of the frustules. In some embodiments, forming the second electrode includes screen printing the second electrode. In some embodiments, forming the second electrode includes forming a membrane of the frustules. In some embodiments, forming the second electrode includes roll-to-roll printing the membrane including the second electrode.

In some embodiments, the method further comprises sorting the frustules according to a property. In some embodiments, the property comprises at least one of shape, dimension, material, and porosity.

In some embodiments, an ink comprises a solution and frustules dispersed in the solution.

In some embodiments, the frustules have a substantially uniform property. In some embodiments, the property comprises shape, for example including a cylinder, a sphere, a disc, or a prism. In some embodiments, the property comprises a dimension, for example including diameter, length, or a longest axis. In some embodiments, the property comprises porosity. In some embodiments, the property comprises mechanical strength.

In some embodiments, the frustules comprise a surface modifying structure. In some embodiments, the surface modifying structure includes a conductive material. In some embodiments, the conductive material includes at least one of silver, aluminum, tantalum, copper, lithium, magnesium, and brass. In some embodiments, the surface modifying structure includes zinc oxide (ZnO). In some embodiments, the surface modifying structure comprises a semiconductor. In some embodiments, the semiconductor includes at least one of silicon, germanium, silicon germanium, and gallium arsenide. In some embodiments, the surface modifying structure comprises at least one of a nanowire, a nanoparticle, and a structure having a rosette shape. In some embodiments, the surface modifying structure is on an exterior surface of the frustules. In some embodiments, the surface modifying structure is on an interior surface of the frustules. In some embodiments, the surface modifying structure is on an interior surface and an exterior surface of the frustules.

In some embodiments, the frustules comprise a surface modifying material. In some embodiments, the surface modifying material comprises a conductive material. In some embodiments, the surface modifying material includes at least one of silver, aluminum, tantalum, copper, lithium, magnesium, and brass. In some embodiments, the surface modifying material includes ZnO. In some embodiments, the surface modifying material includes a semiconductor. In some embodiments, the semiconductor includes at least one of silicon, germanium, silicon germanium, and gallium arsenide. In some embodiments, the surface modifying material is on an exterior surface of the frustules. In some embodiments, the surface modifying material is on an interior surface of the frustules. In some embodiments, the surface modifying material is on an exterior surface and an interior surface of the frustules.

In some embodiments, the ink further comprises a conductive filler. In some embodiments, the conductive filler comprises graphitic carbon. In some embodiments, the conductive filler comprises graphene.

In some embodiments, the ink further comprises an adherence material. In some embodiments, the adherence material comprises a polymer.

In some embodiments, the ink further comprises an electrolyte. In some embodiments, the electrolyte comprises at least one of an ionic liquid, an acid, a base, and a salt. In some embodiments, the electrolyte comprises an electrolytic gel.

In some embodiments, a device comprises at least one of the inks described herein. In some embodiments, the device comprises a printed energy storage device. In some embodiments, the printed energy storage device comprises a capacitor. In some embodiments, the printed energy storage device comprises a supercapacitor. In some embodiments, the printed energy storage device comprises a battery.

A method of extracting a diatom frustule portion may comprise dispersing a plurality of diatom frustule portions in a dispersing solvent. At least one of an organic contaminant and an inorganic contaminant may be removed. The method of extracting a diatom frustule portion may comprise dispersing the plurality of diatom frustule portions in a surfactant, the surfactant reducing an agglomeration of the plurality of diatom frustule portions. The method may comprise extracting a plurality of diatom frustule portions having at least one common characteristic using a disc stack centrifuge.

In some embodiments, the at least one common characteristic can include at least one of a dimension, a shape, a material, and a degree of brokenness. The dimension may include at least one of a length and a diameter.

In some embodiments, a solid mixture can comprise the plurality of diatom frustule portions. The method of extracting a diatom frustule portion may comprise reducing a particle dimension of the solid mixture. Reducing the particle dimension of the solid mixture may be before dispersing the plurality of diatom frustule portions in the dispersing solvent. In some embodiments, reducing the particle dimension can comprise grinding the solid mixture. Grinding the

solid mixture may include applying to the solid mixture at least one of a mortar and a pestle, a jar mill, and a rock crusher.

In some embodiments, a component of the solid mixture having a longest component dimension that is greater than a longest frustule portion dimension of the plurality of diatom frustule portions can be extracted. Extracting the component of the solid mixture may comprise sieving the solid mixture. Sieving the solid mixture may comprise processing the solid mixture with a sieve having a mesh size from about 15 microns to about 25 microns. Sieving the solid mixture may comprise processing the solid mixture with a sieve having a mesh size from about 10 microns to about 25 microns.

In some embodiments, the method of extracting a diatom frustule portion can comprise sorting the plurality of diatom frustule portions to separate a first diatom frustule portion from a second diatom frustule portion, the first diatom frustule portion having a greater longest dimension. For example, the first diatom frustule portion may comprise a plurality of unbroken diatom frustule portions. The second diatom frustule portion may comprise a plurality of broken diatom frustule portions.

In some embodiments, sorting the plurality of diatom frustule portions can comprise filtering the plurality of diatom frustule portions. Filtering may comprise disturbing agglomeration of the plurality of diatom frustule portions. In some embodiments, disturbing agglomeration of the plurality of diatom frustule portions can comprise stirring. In some embodiments, disturbing agglomeration of the plurality of diatom frustule portions can comprise shaking. In some embodiments, disturbing agglomeration of the plurality of diatom frustule portions can comprise bubbling.

Filtering may include applying a sieve to the plurality of diatom frustule portions. For example, the sieve may have a mesh size from about 5 microns to about 10 microns, including about 7 microns.

In some embodiments, the method of extracting a diatom frustule portion can include obtaining a washed diatom frustule portion. Obtaining the washed diatom frustule portion may comprise washing the plurality of diatom frustule portions with a cleaning solvent after removing the at least one of the organic contaminant and the inorganic contaminant. In some embodiments, obtaining the washed diatom frustule portion can comprise washing the diatom frustule portion having the at least one common characteristic with a cleaning solvent.

The cleaning solvent may be removed. For example, removing the cleaning solvent may comprise sedimenting the plurality of diatom frustule portions after removing at least one of the organic contaminant and the inorganic contaminant. For example, removing the cleaning solvent may comprise sedimenting the plurality of diatom frustule portions having the at least one common characteristic. Sedimenting the plurality of diatom frustule portions may comprise centrifuging. In some embodiments, centrifuging can comprise applying a centrifuge suitable for large scale processing. In some embodiments, centrifuging can comprise applying at least one of a disc stack centrifuge, a decanter centrifuge, and a tubular bowl centrifuge.

In some embodiments, at least one of the dispersing solvent and the cleaning solvent can comprise water.

In some embodiments, at least one of dispersing the plurality of diatom frustule portions in the dispersing solvent and dispersing the plurality of diatom frustule portions in the surfactant can comprise sonicating the plurality of diatom frustules.

The surfactant may comprise a cationic surfactant. For example, the cationic surfactant may comprise at least one of a benzalkonium chloride, a cetrimonium bromide, a lauryl methyl gluceth-10 hydroxypropyl dimonium chloride, a benzethonium chloride, a benzethonium chloride, a bronidox, a dmethyldioctadecylammonium chloride, and a tetramethylammonium hydroxide.

The surfactant may comprise a non-ionic surfactant. For example, the non-ionic surfactant may comprise at least one of a cetyl alcohol, a stearyl alcohol, a cetostearyl alcohol, an oleyl alcohol, a polyoxyethylene glycol alkyl ether, an octaethylene glycol monododecyl ether, a glucoside alkyl ethers, a decyl glucoside, a polyoxyethylene glycol octylphenol ethers, an octylphenol ethoxylate (Triton X-100™), a nonoxynol-9, a glyceryl laurate, a polysorbate, and a poloxamer.

In some embodiments, the method of extracting a diatom frustule portion can comprise dispersing the plurality of diatom frustules in an additive component. Dispersing the plurality of diatom frustules in an additive component may be before dispersing the plurality of diatom frustules in the surfactant. Dispersing the plurality of diatom frustules in an additive component may be after dispersing the plurality of diatom frustules in the surfactant. Dispersing the plurality of diatom frustules in an additive component may be at least partially simultaneous with dispersing the plurality of diatom frustules in the surfactant. The additive component may include at least one of a potassium chloride, an ammonium chloride, an ammonium hydroxide, and a sodium hydroxide.

In some embodiments, dispersing the plurality of diatom frustule portions can comprise obtaining a dispersion comprising about 1 weight percent to about 5 weight percent of the plurality of diatom frustule portions.

In some embodiments, removing the organic contaminant can comprise heating the plurality of diatom frustule portions in the presence of a bleach. The bleach may include at least one of a hydrogen peroxide and a nitric acid. Heating the plurality of diatom frustule portions may comprise heating the plurality of diatom frustule portions in a solution comprising an amount of hydrogen peroxide in a range from about 10 volume percent to about 20 volume percent. Heating the plurality of diatom frustule portions may comprise heating the plurality of diatom frustule portions for a duration of about 5 minutes to about 15 minutes.

In some embodiments, removing the organic contaminant can comprise annealing the plurality of diatom frustule portions. In some embodiments, removing the inorganic contaminant can comprise combining the plurality of diatom frustule portions with at least one of a hydrochloric acid and a sulfuric acid. Combining the plurality of diatom frustule portions with at least one of a hydrochloric acid and a sulfuric acid may include mixing the plurality of diatom frustule portions in a solution comprising about 15 volume percent to about 25 volume percent of hydrochloric acid. For example, the mixing may be for a duration of about 20 minutes to about 40 minutes.

A method of extracting a diatom frustule portion may include extracting a plurality of diatom frustule portions having at least one common characteristic using a disc stack centrifuge.

In some embodiments, the method of extracting a diatom frustule portion can comprise dispersing the plurality of diatom frustule portions in a dispersing solvent. In some embodiments, the method can comprise removing at least one of an organic contaminant and an inorganic contaminant. In some embodiments, the method can comprise dispersing the plurality of diatom frustule portions in a

surfactant, the surfactant reducing an agglomeration of the plurality of diatom frustule portions.

The at least one common characteristic may include at least one of a dimension, a shape, a material, and a degree of brokenness. The dimension may include at least one of a length and a diameter.

In some embodiments, a solid mixture can comprise the plurality of diatom frustule portions. The method of extracting a diatom frustule portion may comprise reducing a particle dimension of the solid mixture. Reducing the particle dimension of the solid mixture may be before dispersing the plurality of diatom frustule portions in the dispersing solvent. In some embodiments, reducing the particle dimension can comprise grinding the solid mixture. Grinding the solid mixture may include applying to the solid mixture at least one of a mortar and a pestle, a jar mill, and a rock crusher.

In some embodiments, a component of the solid mixture having a longest component dimension that is greater than a longest frustule portion dimension of the plurality of diatom frustule portions can be extracted. Extracting the component of the solid mixture may comprise sieving the solid mixture. Sieving the solid mixture may comprise processing the solid mixture with a sieve having a mesh size from about 15 microns to about 25 microns. Sieving the solid mixture may comprise processing the solid mixture with a sieve having a mesh size from about 10 microns to about 25 microns.

In some embodiments, the method of extracting a diatom frustule portion can comprise sorting the plurality of diatom frustule portions to separate a first diatom frustule portion from a second diatom frustule portion, the first diatom frustule portion having a greater longest dimension. For example, the first diatom frustule portion may comprise a plurality of unbroken diatom frustule portions. The second diatom frustule portion may comprise a plurality of broken diatom frustule portions.

In some embodiments, sorting the plurality of diatom frustule portions can comprise filtering the plurality of diatom frustule portions. Filtering may comprise disturbing agglomeration of the plurality of diatom frustule portions. In some embodiments, disturbing agglomeration of the plurality of diatom frustule portions can comprise stirring. In some embodiments, disturbing agglomeration of the plurality of diatom frustule portions can comprise shaking. In some embodiments, disturbing agglomeration of the plurality of diatom frustule portions can comprise bubbling.

Filtering may include applying a sieve to the plurality of diatom frustule portions. For example, the sieve may have a mesh size from about 5 microns to about 10 microns, including about 7 microns.

In some embodiments, the method of extracting a diatom frustule portion can include obtaining a washed diatom frustule portion. Obtaining the washed diatom frustule portion may comprise washing the plurality of diatom frustule portions with a cleaning solvent after removing the at least one of the organic contaminant and the inorganic contaminant. In some embodiments, obtaining the washed diatom frustule portion can comprise washing the diatom frustule portion having the at least one common characteristic with a cleaning solvent.

The cleaning solvent may be removed. For example, removing the cleaning solvent may comprise sedimenting the plurality of diatom frustule portions after removing at least one of the organic contaminant and the inorganic contaminant. For example, removing the cleaning solvent may comprise sedimenting the plurality of diatom frustule portions having the at least one common characteristic. Sedimenting the plurality of diatom frustule portions may comprise centrifuging. In some embodiments, centrifuging can comprise applying a centrifuge suitable for large scale processing. In some embodiments, centrifuging can comprise applying at least one of a disc stack centrifuge, a decanter centrifuge, and a tubular bowl centrifuge.

In some embodiments, at least one of the dispersing solvent and the cleaning solvent can comprise water.

In some embodiments, at least one of dispersing the plurality of diatom frustule portions in the dispersing solvent and dispersing the plurality of diatom frustule portions in the surfactant can comprise sonicating the plurality of diatom frustules.

The surfactant may comprise a cationic surfactant. For example, the cationic surfactant may comprise at least one of a benzalkonium chloride, a cetrimonium bromide, a lauryl methyl gluceth-10 hydroxypropyl dimonium chloride, a benzethonium chloride, a benzethonium chloride, a bronidox, a dimethyldioctadecylammonium chloride, and a tetramethylammonium hydroxide.

The surfactant may comprise a non-ionic surfactant. For example, the non-ionic surfactant may comprise at least one of a cetyl alcohol, a stearyl alcohol, a cetostearyl alcohol, an oleyl alcohol, a polyoxyethylene glycol alkyl ether, an octaethylene glycol monododecyl ether, a glucoside alkyl ethers, a decyl glucoside, a polyoxyethylene glycol octylphenol ethers, an octylphenol ethoxylate (Triton X-100™), a nonoxynol-9, a glyceryl laurate, a polysorbate, and a poloxamer.

In some embodiments, the method of extracting a diatom frustule portion can comprise dispersing the plurality of diatom frustules in an additive component. Dispersing the plurality of diatom frustules in an additive component may be before dispersing the plurality of diatom frustules in the surfactant. Dispersing the plurality of diatom frustules in an additive component may be after dispersing the plurality of diatom frustules in the surfactant. Dispersing the plurality of diatom frustules in an additive component may be at least partially simultaneous with dispersing the plurality of diatom frustules in the surfactant. The additive component may include at least one of a potassium chloride, an ammonium chloride, an ammonium hydroxide, and a sodium hydroxide.

In some embodiments, dispersing the plurality of diatom frustule portions can comprise obtaining a dispersion comprising about 1 weight percent to about 5 weight percent of the plurality of diatom frustule portions.

In some embodiments, removing the organic contaminant can comprise heating the plurality of diatom frustule portions in the presence of a bleach. The bleach may include at least one of a hydrogen peroxide and a nitric acid. Heating the plurality of diatom frustule portions may comprise heating the plurality of diatom frustule portions in a solution comprising an amount of hydrogen peroxide in a range from about 10 volume percent to about 20 volume percent. Heating the plurality of diatom frustule portions may comprise heating the plurality of diatom frustule portions for a duration of about 5 minutes to about 15 minutes.

In some embodiments, removing the organic contaminant can comprise annealing the plurality of diatom frustule portions. In some embodiments, removing the inorganic contaminant can comprise combining the plurality of diatom frustule portions with at least one of a hydrochloric acid and a sulfuric acid. Combining the plurality of diatom frustule portions with at least one of a hydrochloric acid and a sulfuric acid may include mixing the plurality of diatom frustule portions in a solution comprising about 15 volume

percent to about 25 volume percent of hydrochloric acid. For example, the mixing may be for a duration of about 20 minutes to about 40 minutes.

A method of extracting a diatom frustule portion may include dispersing a plurality of diatom frustule portions with a surfactant, the surfactant reducing an agglomeration of the plurality of diatom frustule portions.

The method of extracting a diatom frustule portion may include extracting a plurality of diatom frustule portions having at least one common characteristic using a disc stack centrifuge. In some embodiments, the method of extracting a diatom frustule portion can comprise dispersing a plurality of diatom frustule portions in a dispersing solvent. In some embodiments, at least one of an organic contaminant and an inorganic contaminant may be removed.

In some embodiments, the at least one common characteristic can include at least one of a dimension, a shape, a material, and a degree of brokenness. The dimension may include at least one of a length and a diameter.

In some embodiments, a solid mixture can comprise the plurality of diatom frustule portions. The method of extracting a diatom frustule portion may comprise reducing a particle dimension of the solid mixture. Reducing the particle dimension of the solid mixture may be before dispersing the plurality of diatom frustule portions in the dispersing solvent. In some embodiments, reducing the particle dimension can comprise grinding the solid mixture. Grinding the solid mixture may include applying to the solid mixture at least one of a mortar and a pestle, a jar mill, and a rock crusher.

In some embodiments, a component of the solid mixture having a longest component dimension that is greater than a longest frustule portion dimension of the plurality of diatom frustule portions can be extracted. Extracting the component of the solid mixture may comprise sieving the solid mixture. Sieving the solid mixture may comprise processing the solid mixture with a sieve having a mesh size from about 15 microns to about 25 microns. Sieving the solid mixture may comprise processing the solid mixture with a sieve having a mesh size from about 10 microns to about 25 microns.

In some embodiments, the method of extracting a diatom frustule portion can comprise sorting the plurality of diatom frustule portions to separate a first diatom frustule portion from a second diatom frustule portion, the first diatom frustule portion having a greater longest dimension. For example, the first diatom frustule portion may comprise a plurality of unbroken diatom frustule portions. The second diatom frustule portion may comprise a plurality of broken diatom frustule portions.

In some embodiments, sorting the plurality of diatom frustule portions can comprise filtering the plurality of diatom frustule portions. Filtering may comprise disturbing agglomeration of the plurality of diatom frustule portions. In some embodiments, disturbing agglomeration of the plurality of diatom frustule portions can comprise stirring. In some embodiments, disturbing agglomeration of the plurality of diatom frustule portions can comprise shaking. In some embodiments, disturbing agglomeration of the plurality of diatom frustule portions can comprise bubbling.

Filtering may include applying a sieve to the plurality of diatom frustule portions. For example, the sieve may have a mesh size from about 5 microns to about 10 microns, including about 7 microns.

In some embodiments, the method of extracting a diatom frustule portion can include obtaining a washed diatom frustule portion. Obtaining the washed diatom frustule portion may comprise washing the plurality of diatom frustule portions with a cleaning solvent after removing the at least one of the organic contaminant and the inorganic contaminant. In some embodiments, obtaining the washed diatom frustule portion can comprise washing the diatom frustule portion having the at least one common characteristic with a cleaning solvent.

The cleaning solvent may be removed. For example, removing the cleaning solvent may comprise sedimenting the plurality of diatom frustule portions after removing at least one of the organic contaminant and the inorganic contaminant. For example, removing the cleaning solvent may comprise sedimenting the plurality of diatom frustule portions having the at least one common characteristic. Sedimenting the plurality of diatom frustule portions may comprise centrifuging. In some embodiments, centrifuging can comprise applying a centrifuge suitable for large scale processing. In some embodiments, centrifuging can comprise applying at least one of a disc stack centrifuge, a decanter centrifuge, and a tubular bowl centrifuge.

In some embodiments, at least one of the dispersing solvent and the cleaning solvent can comprise water.

In some embodiments, at least one of dispersing the plurality of diatom frustule portions in the dispersing solvent and dispersing the plurality of diatom frustule portions in the surfactant can comprise sonicating the plurality of diatom frustules.

The surfactant may comprise a cationic surfactant. For example, the cationic surfactant may comprise at least one of a benzalkonium chloride, a cetrimonium bromide, a lauryl methyl gluceth-10 hydroxypropyl dimonium chloride, a benzethonium chloride, a benzethonium chloride, a bronidox, a dimethyldioctadecylammonium chloride, and a tetramethylammonium hydroxide.

The surfactant may comprise a non-ionic surfactant. For example, the non-ionic surfactant may comprise at least one of a cetyl alcohol, a stearyl alcohol, a cetostearyl alcohol, an oleyl alcohol, a polyoxyethylene glycol alkyl ether, an octaethylene glycol monododecyl ether, a glucoside alkyl ethers, a decyl glucoside, a polyoxyethylene glycol octylphenol ethers, an octylphenol ethoxylate (Triton X-100™), a nonoxynol-9, a glyceryl laurate, a polysorbate, and a poloxamer.

In some embodiments, the method of extracting a diatom frustule portion can comprise dispersing the plurality of diatom frustules in an additive component. Dispersing the plurality of diatom frustules in an additive component may be before dispersing the plurality of diatom frustules in the surfactant. Dispersing the plurality of diatom frustules in an additive component may be after dispersing the plurality of diatom frustules in the surfactant. Dispersing the plurality of diatom frustules in an additive component may be at least partially simultaneous with dispersing the plurality of diatom frustules in the surfactant. The additive component may include at least one of a potassium chloride, an ammonium chloride, an ammonium hydroxide, and a sodium hydroxide.

In some embodiments, dispersing the plurality of diatom frustule portions can comprise obtaining a dispersion comprising about 1 weight percent to about 5 weight percent of the plurality of diatom frustule portions.

In some embodiments, removing the organic contaminant can comprise heating the plurality of diatom frustule portions in the presence of a bleach. The bleach may include at least one of a hydrogen peroxide and a nitric acid. Heating the plurality of diatom frustule portions may comprise heating the plurality of diatom frustule portions in a solution comprising an amount of hydrogen peroxide in a range from about 10 volume percent to about 20 volume percent.

Heating the plurality of diatom frustule portions may comprise heating the plurality of diatom frustule portions for a duration of about 5 minutes to about 15 minutes.

In some embodiments, removing the organic contaminant can comprise annealing the plurality of diatom frustule portions. In some embodiments, removing the inorganic contaminant can comprise combining the plurality of diatom frustule portions with at least one of a hydrochloric acid and a sulfuric acid. Combining the plurality of diatom frustule portions with at least one of a hydrochloric acid and a sulfuric acid may include mixing the plurality of diatom frustule portions in a solution comprising about 15 volume percent to about 25 volume percent of hydrochloric acid. For example, the mixing may be for a duration of about 20 minutes to about 40 minutes.

A method of forming silver nanostructures on a diatom frustule portion may include forming a silver seed layer on a surface of the diatom frustule portion. The method may include forming a nanostructure on the seed layer.

In some embodiments, the nanostructures can comprise at least one of a coating, a nanowire, a nanoplate, a dense array of nanoparticles, a nanobelt, and a nanodisk. In some embodiments, the nanostructures can comprise silver.

Forming the silver seed layer may comprise applying a cyclic heating regimen to a first silver contributing component and the diatom frustule portion. In some embodiments, applying the cyclic heating regimen can comprise applying a cyclic microwave power. Applying the cyclic microwave power may comprise alternating a microwave power between about 100 Watt and 500 Watt. For example, alternating may comprise alternating the microwave power every minute. In some embodiments, alternating can comprise alternating the microwave power for a duration of about 30 minutes. In some embodiments, alternating can comprise alternating the microwave power for a duration of about 20 minutes to about 40 minutes.

In some embodiments, forming the silver seed layer can comprise combining the diatom frustule portion with a seed layer solution. The seed layer solution may include the first silver contributing component and a seed layer reducing agent. For example, the seed layer reducing agent may be a seed layer solvent. In some embodiments, the seed layer reducing agent and the seed layer solvent can comprise a polyethylene glycol.

In some embodiments, the seed layer solution can comprise the first silver contributing component, a seed layer reducing agent and a seed layer solvent.

Forming the silver seed layer may comprise mixing the diatom frustule portion with the seed layer solution. In some embodiments, the mixing can comprise ultrasonicating.

In some embodiments, the seed layer reducing agent can comprise a N,N-Dimethylformamide, the first silver contributing component can comprise a silver nitrate, and the seed layer solvent can comprise at least one of a water and a polyvinylpyrrolidone.

Forming the nanostructure may comprise combining the diatom frustule portion with a nanostructure forming reducing agent. In some embodiments, forming the nanostructure further may include heating the diatom frustule portion after combining the diatom frustule portion with the nanostructure forming reducing agent. For example, the heating may comprise heating to a temperature of about 120° C. to about 160° C.

In some embodiments, forming the nanostructure can include titrating the diatom frustule portion with a titration solution comprising a nanostructure forming solvent and a second silver contributing component. In some embodiments, forming the nanostructure can comprise mixing after titrating the diatom frustule portion with the titration solution.

In some embodiments, at least one of the seed layer reducing agent and the nanostructure forming reducing agent can comprise at least one of a hydrazine, a formaldehyde, a glucose, sodium tartrate, an oxalic acid, a formic acid, an ascorbic acid, and an ethylene glycol.

In some embodiments, at least one of the first silver contributing component and the second silver contributing component can comprise at least one of a silver salt and a silver oxide. For example, the silver salt may include at least one of a silver nitrate and an ammoniacal silver nitrate, a silver chloride (AgCl), a silver cyanide (AgCN), a silver tetrafluoroborate, a silver hexafluorophosphate, and a silver ethylsulphate.

Forming the nanostructure may be in an ambient to reduce oxide formation. For example, the ambient may comprise an argon atmosphere.

In some embodiments, at least one of the seed layer solvent and the nanostructure forming solvent can comprise at least one of a propylene glycol, a water, a methanol, an ethanol, a 1-propanol, a 2-propanol a 1-methoxy-2-propanol, a 1-butanol, a 2-butanol a 1-pentanol, a 2-pentanol, a 3-pentanol, a 1-hexanol, a 2-hexanol, a 3-hexanol, an octanol, a 1-octanol, a 2-octanol, a 3-octanol, a tetrahydrofurfuryl alcohol (THFA), a cyclohexanol, a cyclopentanol, a terpineol, a butyl lactone; a methyl ethyl ether, a diethyl ether, an ethyl propyl ether, a polyethers, a diketones, a cyclohexanone, a cyclopentanone, a cycloheptanone, a cyclooctanone, an acetone, a benzophenone, an acetylacetone, an acetophenone, a cyclopropanone, an isophorone, a methyl ethyl ketone, an ethyl acetate, a dimethyl adipate, a propylene glycol monomethyl ether acetate, a dimethyl glutarate, a dimethyl succinate, a glycerin acetate, a carboxylates, a propylene carbonate, a glycerin, a diol, a triol, a tetraol, a pentanol, an ethylene glycol, a diethylene glycol, a polyethylene glycol, a propylene glycol, a dipropylene glycol, a glycol ether, a glycol ether acetate, a 1,4-butanediol, a 1,2-butanediol, a 2,3-butanediol, a 1,3-propanediol, a 1,4-butanediol, a 1,5-pentanediol, a 1,8-octanediol, a 1,2-propanediol, a 1,3-butanediol, a 1,2-pentanediol, an etohexadiol, a p-menthane-3,8-diol, a 2-methyl-2,4-pentanediol, a tetramethyl urea, a n-methylpyrrolidone, an acetonitrile, a tetrahydrofuran (THF), a dimethyl formamide (DMF), a N-methyl formamide (NMF), a dimethyl sulfoxide (DMSO), a thionyl chloride and a sulfuryl chloride.

The diatom frustule portion may comprise a broken diatom frustule portion. The diatom frustule portion may comprise an unbroken diatom frustule portion. In some embodiments, the diatom frustule portion can be obtained through a diatom frustule portion separation process. For example, the process may comprise at least one of using a surfactant to reduce an agglomeration of a plurality of diatom frustule portions and using a disc stack centrifuge.

A method of forming zinc-oxide nanostructures on a diatom frustule portion may include forming a zinc-oxide seed layer on a surface of the diatom frustule portion. The method may comprise forming a nanostructure on the zinc-oxide seed layer.

In some embodiments, the nanostructure can comprise at least one of a nanowire, a nanoplate, a dense array of nanoparticles, a nanobelt, and a nanodisk. In some embodiments, the nanostructures can comprise zinc-oxide.

Forming the zinc-oxide seed layer may comprise heating a first zinc contributing component and the diatom frustule portion. In some embodiments, heating the first zinc con-

tributing component and the diatom frustule portion can comprise heating to a temperature in a range from about 175° C. to about 225° C.

In some embodiments, forming the nanostructure can comprise applying a heating regimen to the diatom frustule portion having the zinc-oxide seed layer in the presence of a nanostructure forming solution comprising a second zinc contributing component. The heating regimen may comprise heating to a nanostructure forming temperature. For example, the nanostructure forming temperature may be from about 80° C. to about 100° C. In some embodiments, the heating may be for a duration of about one to about three hours. In some embodiments, the heating regimen can comprise applying a cyclic heating routine. For example, the cyclic heating routine may include applying a microwave heating to the diatom frustule portion having the zinc-oxide seed layer for a heating duration and then turning the microwaving heating off for a cooling duration, for a total cyclic heating duration. In some embodiments, the heating duration can be about 1 minute to about 5 minutes. In some embodiments, the cooling duration can be about 30 seconds to about 5 minutes. The total cyclic heating duration may be about 5 minutes to about 20 minutes. Applying the microwave heating may include applying about 480 Watt to about 520 Watt of microwave power, including about 80 Watt to about 120 Watt of microwave power.

In some embodiments, at least one of the first zinc contributing component and the second zinc contributing component can comprise at least one of a zinc acetate, a zinc acetate hydrate, a zinc nitrate, a zinc nitrate hexahydrate, a zinc chloride, a zinc sulfate, and a sodium zincate.

In some embodiments, the nanostructure forming solution may include a base. For example, the base may comprise at least one of a sodium hydroxide, an ammonium hydroxide, potassium hydroxide, a tetramethylammonium hydroxide, a lithium hydroxide, a hexamethylenetetramine, an ammonia solution, a sodium carbonate, and a ethylenediamine.

In some embodiments, forming the nanostructure can comprise adding an additive component. The additive component may include at least one of a tributylamine, a triethylamine, a triethanolamine, a diisopropylamine, an ammonium phosphate, a 1,6-hexadianol, a triethyldiethylnol, an isopropylamine, a cyclohexylamine, a n-butylamine, an ammonium chloride, a hexamethylenetetramine, an ethylene glycol, an ethanolamine, a polyvinylalcohol, a polyethylene glycol, a sodium dodecyl sulphate, a cetyltrimethyl ammonium bromide, and a carbamide.

In some embodiments, at least one of the nanostructure forming solution and a zinc-oxide seed layer forming solution can comprise a solvent, the solvent comprising at least one of a propylene glycol, a water, a methanol, an ethanol, a 1-propanol, a 2-propanol a 1-methoxy-2-propanol, a 1-butanol, a 2-butanol a 1-pentanol, a 2-pentanol, a 3-pentanol, a 1-hexanol, a 2-hexanol, a 3-hexanol, an octanol, a 1-octanol, a 2-octanol, a 3-octanol, a tetrahydrofurfuryl alcohol (THFA), a cyclohexanol, a cyclopentanol, a terpineol, a butyl lactone; a methyl ethyl ether, a diethyl ether, an ethyl propyl ether, a polyethers, a diketones, a cyclohexanone, a cyclopentanone, a cycloheptanone, a cyclooctanone, an acetone, a benzophenone, an acetylacetone, an acetophenone, a cyclopropanone, an isophorone, a methyl ethyl ketone, an ethyl acetate, a dimethyl adipate, a propylene glycol monomethyl ether acetate, a dimethyl glutarate, a dimethyl succinate, a glycerin acetate, a carboxylates, a propylene carbonate, a glycerin, a diol, a triol, a tetraol, a pentanol, an ethylene glycol, a diethylene glycol, a polyethylene glycol, a propylene glycol, a dipropylene glycol, a glycol ether, a glycol ether acetate, a 1,4-butanediol, a 1,2-butanediol, a 2,3-butanediol, a 1,3-propanediol, a 1,4-butanediol, a 1,5-pentanediol, a 1,8-octanediol, a 1,2-propanediol, a 1,3-butanediol, a 1,2-pentanediol, an etohexadiol, a p-menthane-3,8-diol, a 2-methyl-2,4-pentanediol, a tetramethyl urea, a n-methylpyrrolidone, an acetonitrile, a tetrahydrofuran (THF), a dimethyl formamide (DMF), a N-methyl formamide (NMF), a dimethyl sulfoxide (DMSO), a thionyl chloride and a sulfuryl chloride.

The diatom frustule portion may comprise a broken diatom frustule portion. The diatom frustule portion may comprise an unbroken diatom frustule portion. In some embodiments, the diatom frustule portion can be obtained through a diatom frustule portion separation process. For example, the process may comprise at least one of using a surfactant to reduce an agglomeration of a plurality of diatom frustule portions and using a disc stack centrifuge.

A method of forming carbon nanostructures on a diatom frustule portion may include forming a metal seed layer on a surface of the diatom frustule portion. The method may include forming a carbon nanostructure on the seed layer.

In some embodiments, the carbon nanostructure can comprise a carbon nanotube. The carbon nanotube may comprise at least one of a single-walled carbon nanotube and a multi-walled carbon nanotube.

In some embodiments, forming the metal seed layer can comprise spray coating the surface of the diatom frustule portion. In some embodiments, forming the metal seed layer can comprise introducing the surface of the diatom frustule portion to at least one of a liquid comprising the metal, a gas comprising the metal and the solid comprising a metal.

In some embodiments, forming the carbon nanostructure can comprise using chemical vapor deposition (CVD). Forming the carbon nanostructure can comprise exposing the diatom frustule portion to a nanostructure forming reducing gas after exposing the diatom frustule portion to a nanostructure forming carbon gas. Forming the carbon nanostructure may comprise exposing the diatom frustule portion to a nanostructure forming reducing gas before exposing the diatom frustule portion to a nanostructure forming carbon gas. In some embodiments, forming the carbon nanostructure comprises exposing the diatom frustule portion to a nanostructure forming gas mixture comprising a nanostructure forming reducing gas and a nanostructure forming carbon gas. The nanostructure forming gas mixture may include a neutral gas. For example, the neutral gas may be argon.

In some embodiments, the metal can comprise at least one of a nickel, an iron, a cobalt, a cobalt-molybdenum bimetallic, a copper, a gold, a silver, a platinum, a palladium, a manganese, an aluminum, a magnesium, a chromium, an antimony, an aluminum-iron-molybdenum (Al/Fe/Mo), an iron pentacarbonyl ($Fe(CO)_5$), an iron (III) nitrate hexahydrate ($(Fe(NO_3)_3.6H_2O$), a cobalt (II) chloride hexahydrate ($CoCl_2.6H_2O$), an ammonium molybdate tetrahydrate ($(NH_4)_6Mo_7O_{24}.4H_2O$), a molybdenum (VI) dichloride dioxide MoO_2Cl_2, and an alumina nanopowder.

In some embodiments, the nanostructure forming reducing gas can comprise at least one of an ammonia, a nitrogen, and a hydrogen. The nanostructure forming carbon gas may comprise at least one of an acetylene, an ethylene, an ethanol, a methane, a carbon oxide, and a benzene.

In some embodiments, forming the metal seed layer can comprise forming a silver seed layer. Forming the silver seed layer may comprise forming a silver nanostructure on the surface of the diatom frustule portion.

The diatom frustule portion may comprise a broken diatom frustule portion. The diatom frustule portion may comprise an unbroken diatom frustule portion. In some embodiments, the diatom frustule portion can be obtained through a diatom frustule portion separation process. For example, the process may comprise at least one of using a surfactant to reduce an agglomeration of a plurality of diatom frustule portions and using a disc stack centrifuge.

A method of fabricating a silver ink may include combining an ultraviolet light sensitive component and a plurality of diatom frustule portions having a silver nanostructure on a surface of the plurality of diatom frustule portions, the surface comprising a plurality of perforations.

In some embodiments, the method of fabricating the silver ink can comprise forming a silver seed layer on the surface of the plurality of diatom frustule portions. In some embodiments, the method can include forming the silver nanostructure on the seed layer.

The plurality of diatom frustule portions may include a plurality of broken diatom frustule portions. The plurality of diatom frustule portions may include a plurality of diatom frustule flakes.

In some embodiments, the silver ink is depositable in a layer having a thickness of about 5 microns to about 15 microns after curing. In some embodiments, at least one of the plurality of perforations has a diameter of about 250 nanometers to about 350 nanometers. In some embodiments, the silver nanostructure can comprise a thickness of about 10 nanometers to about 500 nanometers. The silver ink may comprise an amount of diatom frustules within a range of about 50 weight percent to about 80 weight percent.

Forming the silver seed layer may include forming the silver seed layer on a surface within the plurality of perforations to form a plurality of silver seed plated perforations. Forming the silver seed layer may include forming the silver seed layer on substantially all surfaces of the plurality of diatom frustule portions.

In some embodiments, forming the silver nanostructure may comprise forming the silver nanostructure on a surface within the plurality of perforations to form a plurality of silver nanostructure plated perforations. Forming the silver nanostructure may comprise forming the silver nanostructure on substantially all surfaces of the plurality of diatom frustule portions.

In some embodiments, the ultraviolet light sensitive component can be sensitive to an optical radiation having a wavelength shorter than a dimension of the plurality of perforations. The ultraviolet light sensitive component may be sensitive to an optical radiation having a wavelength shorter than a dimension of at least one of the plurality of silver seed plated perforations and the plurality of silver nanostructure plated perforations.

In some embodiments, combining the plurality of diatom frustule portions with the ultraviolet light sensitive component can include combining the plurality of diatom frustule portions with a photoinitiation synergist agent. For example, the photoinitiation synergist agent may comprise at least one of an ethoxylated hexanediol acrylate, a propoxylated hexanediol acrylate, an ethoxylated trimethylpropane triacrylate, a triallyl cyanurate and an acrylated amine.

In some embodiments, combining the plurality of diatom frustule portions with the ultraviolet light sensitive component can include combining the plurality of diatom frustule portions with a photoinitiator agent. The photoinitiator agent may include at least one of a 2-methyl-1-(4-methylthio) phenyl-2-morpholinyl-1-propanone and an isopropyl thioxanthone.

In some embodiments, combining the plurality of diatom frustule portions with the ultraviolet light sensitive component can include combining the plurality of diatom frustule portions with a polar vinyl monomer. For example, the polar vinyl monomer may include at least one of a n-vinylpyrrolidone and a n-vinylcaprolactam.

The method of fabricating the silver ink may comprise combining the plurality of diatom frustule portions with a rheology modifying agent. In some embodiments, the method of fabricating the silver ink can comprise combining the plurality of diatom frustule portions with a crosslinking agent. In some embodiments, the method can include combining the plurality of diatom frustule portions with a flow and level agent. In some embodiments, the method can include combining the plurality of diatom frustule portions with at least one of an adhesion promoting agent, a wetting agent, and a viscosity reducing agent.

The silver nanostructure may include at least one of a coating, a nanowire, a nanoplate, a dense array of nanoparticles, a nanobelt, and a nanodisk.

In some embodiments, forming the silver seed layer can comprise applying a cyclic heating regimen to a first silver contributing component and the plurality of diatom frustule portions.

Forming the silver seed layer may comprise combining the diatom frustule portion with a seed layer solution. For example, the seed layer solution may comprise the first silver contributing component and a seed layer reducing agent.

Forming the silver nanostructure may comprise combining the diatom frustule portion with a nanostructure forming reducing agent. In some embodiments, forming the silver nanostructure can comprise heating the diatom frustule portion after combining the diatom frustule portion with the nanostructure forming reducing agent. In some embodiments, forming the silver nanostructure can comprise titrating the diatom frustule portion with a titration solution comprising a nanostructure forming solvent and a second silver contributing component.

In some embodiments, the plurality of diatom frustule portions can be obtained through a diatom frustule portion separation process. For example, the process may include at least one of using a surfactant to reduce an agglomeration of a plurality of diatom frustule portions and using a disc stack centrifuge.

A conductive silver ink may include an ultraviolet light sensitive component. The conductive ink may include a plurality of diatom frustule portions having a silver nanostructure on a surface of the plurality of diatom frustule portions, the surface comprising a plurality of perforations.

The plurality of diatom frustule portions may include a plurality of broken diatom frustule portions. The plurality of diatom frustule portions may include a plurality of diatom frustule flakes.

In some embodiments, the silver ink is depositable in a layer having a thickness of about 5 microns to about 15 microns (e.g., after curing). In some embodiments, at least one of the plurality of perforations has a diameter of about 250 nanometers to about 350 nanometers. In some embodiments, the silver nanostructure can comprise a thickness of about 10 nanometers to about 500 nanometers. The silver ink may comprise an amount of diatom frustules within a range of about 50 weight percent to about 80 weight percent.

In some embodiments, at least one of the plurality of perforations can comprise a surface having a silver nanostructure.

In some embodiments, at least one of the plurality of perforations comprises a surface having a silver seed layer. In some embodiments, substantially all surfaces of the plurality of diatom frustule portions can comprise a silver nanostructure.

In some embodiments, the ultraviolet light sensitive component can be sensitive to an optical radiation having a wavelength shorter than a dimension of the plurality of perforations.

In some embodiments, the conductive silver ink can be curable by an ultraviolet radiation. In some embodiments, the plurality of perforations can have a dimension sufficient to allow the ultraviolet radiation to pass through. The conductive silver ink may be depositable in a layer having a thickness of about 5 microns to about 15 microns (e.g., after curing).

In some embodiments, the conductive silver ink can be thermally curable.

The ultraviolet light sensitive component may include a photoinitiation synergist agent. For example, the photoinitiation synergist agent may comprise at least one of an ethoxylated hexanediol acrylate, a propoxylated hexanediol acrylate, an ethoxylated trimethylpropane triacrylate, a triallyl cyanurate and an acrylated amine.

The ultraviolet light sensitive component may include a photoinitiator agent. The photoinitiator agent may include at least one of a 2-methyl-1-(4-methylthio)phenyl-2-morpholinyl-1-propanone and an isopropyl thioxanthone.

In some embodiments, the ultraviolet light sensitive component can include a polar vinyl monomer. For example, the polar vinyl monomer may include at least one of a n-vinyl-pyrrolidone and a n-vinylcaprolactam.

The conductive silver ink may include at least one of a rheology modifying agent, a crosslinking agent, a flow and level agent, a adhesion promoting agent, a wetting agent, and a viscosity reducing agent. In some embodiments, the silver nanostructure can comprise at least one of a coating, a nanowire, a nanoplate, a dense array of nanoparticles, a nanobelt, and a nanodisk.

A method of fabricating a silver film may include curing a mixture comprising an ultraviolet light sensitive component and a plurality of diatom frustule portions having a silver nanostructure on a surface of the plurality of diatom frustule portions, the surface comprising a plurality of perforations.

In some embodiments, the method of fabricating the silver film can comprise forming a silver seed layer on the surface of the plurality of diatom frustule portions. In some embodiments, the method can comprise forming the silver nanostructure on the seed layer. In some embodiments, the method can include combining the plurality of diatom frustule portions with the ultraviolet light sensitive component to form a silver ink.

The plurality of diatom frustule portions may comprise a plurality of broken diatom frustule portions. The plurality of diatom frustule portions may comprise a plurality of diatom frustule flakes.

In some embodiments, the silver ink is depositable in a layer having a thickness of about 5 microns to about 15 microns (e.g., after curing). In some embodiments, at least one of the plurality of perforations has a diameter of about 250 nanometers to about 350 nanometers. In some embodiments, the silver nanostructure can comprise a thickness of about 10 nanometers to about 500 nanometers. The silver ink may comprise an amount of diatom frustules within a range of about 50 weight percent to about 80 weight percent.

Forming the silver seed layer may comprise forming the silver seed layer on a surface within the plurality of perforations to form a plurality of silver seed plated perforations. Forming the silver seed layer may comprise forming the silver seed layer on substantially all surfaces of the plurality of diatom frustule portions.

Forming the silver nanostructure may comprise forming the silver nanostructure on a surface within the plurality of perforations to form a plurality of silver nanostructure plated perforations. Forming the silver nanostructure may comprise forming the silver nanostructure on substantially all surfaces of the plurality of diatom frustule portions.

In some embodiments, curing the mixture can comprise exposing the mixture to an ultraviolet light having a wavelength shorter than a dimension of the plurality of perforations. In some embodiments, curing the mixture can comprise exposing the mixture to an ultraviolet light having a wavelength shorter than a dimension of at least one of the plurality of silver seed plated perforations and the plurality of silver nanostructure plated perforations.

In some embodiments, curing the mixture can comprise thermally curing the mixture.

The ultraviolet light sensitive component may be sensitive to an optical radiation having a wavelength shorter than a dimension of the plurality of perforations. In some embodiments, the ultraviolet light sensitive component can be sensitive to an optical radiation having a wavelength shorter than a dimension of at least one of the plurality of silver seed plated perforations and the plurality of silver nanostructure plated perforations.

Combining the plurality of diatom frustule portions with the ultraviolet light sensitive component may comprise combining the plurality of diatom frustule portions with a photoinitiation synergist agent. For example, the photoinitiation synergist agent may include at least one of an ethoxylated hexanediol acrylate, a propoxylated hexanediol acrylate, an ethoxylated trimethylpropane triacrylate, a triallyl cyanurate and an acrylated amine.

In some embodiments, combining the plurality of diatom frustule portions with the ultraviolet light sensitive component can comprise combining the plurality of diatom frustule portions with a photoinitiator agent. The photoinitiator agent may include at least one of a 2-methyl-1-(4-methylthio) phenyl-2-morpholinyl-1-propanone and an isopropyl thioxanthone.

In some embodiments, combining the plurality of diatom frustule portions with the ultraviolet light sensitive component can comprise combining the plurality of diatom frustule portions with a polar vinyl monomer. The polar vinyl monomer may include at least one of a n-vinyl-pyrrolidone and a n-vinylcaprolactam.

The method of fabricating the conductive silver ink may include combining the plurality of diatom frustule portions with a rheology modifying agent. In some embodiments, the method of fabricating the conductive silver ink can include combining the plurality of diatom frustule portions with a crosslinking agent. In some embodiments, the method can comprise combining the plurality of diatom frustule portions with a flow and level agent. The method may include combining the plurality of diatom frustule portions with at least one of an adhesion promoting agent, a wetting agent, and a viscosity reducing agent.

In some embodiments, the silver nanostructure can comprise at least one of a coating, a nanowire, a nanoplate, a dense array of nanoparticles, a nanobelt, and a nanodisk.

In some embodiments, forming the silver seed layer can comprise applying a cyclic heating regimen to a first silver contributing component and the plurality of diatom frustule portions.

Forming the silver seed layer may comprise combining the diatom frustule portion with a seed layer solution. For example, the seed layer solution may comprise the first silver contributing component and a seed layer reducing agent.

Forming the silver nanostructure may comprise combining the diatom frustule portion with a nanostructure forming reducing agent. In some embodiments, forming the silver nanostructure can comprise heating the diatom frustule portion after combining the diatom frustule portion with the nanostructure forming reducing agent. In some embodiments, forming the silver nanostructure can comprise titrating the diatom frustule portion with a titration solution comprising a nanostructure forming solvent and a second silver contributing component.

In some embodiments, the plurality of diatom frustule portions can be obtained through a diatom frustule portion separation process. For example, the process may include at least one of using a surfactant to reduce an agglomeration of a plurality of diatom frustule portions and using a disc stack centrifuge.

A conductive silver film may include a plurality of diatom frustule portions having a silver nanostructure on a surface of each of the plurality of diatom frustule portions, the surface comprising a plurality of perforations.

In some embodiments, the plurality of diatom frustule portions can comprise a plurality of broken diatom frustule portion. The plurality of diatom frustule portions may include a plurality of diatom frustule flakes.

In some embodiments, at least one of the plurality of perforations has a diameter of about 250 nanometers to about 350 nanometers. In some embodiments, the silver nanostructure can comprise a thickness of about 10 nanometers to about 500 nanometers.

In some embodiments, at least one of the plurality of perforations can comprise a surface having a silver nanostructure. In some embodiments, at least one of the plurality of perforations can comprise a surface having a silver seed layer. Substantially all surfaces of the plurality of diatom frustule portions may comprise a silver nanostructure.

In some embodiments, the silver nanostructure can comprise at least one of a coating, a nanowire, a nanoplate, a dense array of nanoparticles, a nanobelt, and a nanodisk.

In some embodiments, the conductive silver film can comprise a binder resin.

A printed energy storage device can include a first electrode, a second electrode, and a separator between the first electrode and the second electrode, where at least one of the first electrode and the second electrode can include a plurality of frustules having manganese-containing nanostructures.

In some embodiments, the frustules have a substantially uniform property, the substantially uniform property including at least one of a frustule shape, a frustule dimension, a frustule porosity, a frustule mechanical strength, a frustule material, and a degree of brokenness of a frustule.

In some embodiments, the manganese-containing nanostructures can include an oxide of manganese. The oxide of manganese may include manganese(II,III) oxide. The oxide of manganese may include manganese oxyhydroxide.

In some embodiments, at least one of the first electrode and the second electrode can include frustules having zinc-oxide nanostructures. The zinc-oxide nanostructures can include at least one of a nano-wire and a nano-plate.

In some embodiments, the manganese-containing nanostructures cover substantially all surfaces of the frustules. In some embodiments, manganese-containing nanostructures cover some surfaces of the frustules and carbon-containing nanostructures cover other surfaces of the frustules, the manganese-containing nanostructures interspersed with the carbon-containing nanostructures.

A membrane of an energy storage device can include frustules having manganese-containing nanostructures.

In some embodiments, the manganese-containing nanostructures can include an oxide of manganese. The oxide of manganese may include manganese(II,III) oxide. The oxide of manganese may include manganese oxyhydroxide. In some embodiments, manganese-containing nanostructures cover some surfaces of the frustules and carbon-containing nanostructures cover other surfaces of the frustules, the manganese-containing nanostructures interspersed with the carbon-containing nanostructures.

In some embodiments, at least some of the manganese-containing nanostructures can be a nano-fiber. In some embodiments, at least some of the manganese-containing nanostructures have a tetrahedral shape.

In some embodiments, the energy storage device includes a zinc-manganese battery.

An ink for a printed film can include a solution, and frustules having manganese-containing nanostructures dispersed in the solution.

In some embodiments, the manganese-containing nanostructures can include an oxide of manganese. In some embodiments, the manganese-containing nanostructures can include at least one of MnO_2, MnO, Mn_2O_3, MnOOH, and Mn_3O_4.

In some embodiments, at least some of the manganese-containing nanostructures can include a nano-fiber. In some embodiments, at least some of the manganese-containing nanostructures have a tetrahedral shape.

In some embodiments, manganese-containing nanostructures cover some surfaces of the frustules and carbon-containing nanostructures cover other surfaces of the frustules, the manganese-containing nanostructures interspersed with the carbon-containing nano structures.

In some embodiments, an energy storage device can include a cathode having a first plurality of frustules, the first plurality of frustules having nanostructures including an oxide of manganese; and an anode having a second plurality of frustules, the second plurality of frustules having nanostructures including zinc oxide. In some embodiments, the device can be a rechargeable battery.

In some embodiments, the oxide of manganese includes MnO. In some embodiments, the oxide of manganese includes at least one of Mn_3O_4, Mn_2O_3, and MnOOH.

In some embodiments, at least one of the first plurality of frustules includes a ratio of a mass of the oxide of manganese to a mass of the at least one frustule of about 1:20 to about 20:1. In some embodiments, at least one of the second plurality of frustules includes a ratio of a mass of the zinc oxide to a mass of the at least one frustule of about 1:20 to about 20:1.

In some embodiments, the anode can include an electrolyte salt. The electrolyte salt may include a zinc salt.

In some embodiments, at least one of the cathode and the anode can include carbon nanotubes. In some embodiments, at least one of the cathode and the anode can include a conductive filler. The conductive filler may include graphite.

In some embodiments, the energy storage device can have a separator between the cathode and the anode, where the separator includes a third plurality of frustules. The third plurality of frustules may have substantially no surface modifications.

In some embodiments, at least one of the cathode, the anode, and the separator can include an ionic liquid.

In some embodiments, the first plurality of frustules having a first plurality of pores substantially not occluded by the nanostructures including the oxide of manganese, and where the second plurality of frustules has a second plurality of pores substantially not occluded by the nanostructures including the zinc oxide.

In some embodiments, a frustule can include a plurality of nanostructures on at least one surface, where the plurality of nanostructures includes zinc oxide, and where a ratio of a mass of the plurality of nanostructures to a mass of the frustule is about 1:1 to about 20:1. In some embodiments, the plurality of nanostructures includes at least one of nanowires, nanoplates, dense nanoparticles, nanobelts, and nanodisks. In some embodiments, the frustule includes a plurality of pores substantially not occluded by the plurality of nanostructures.

In some embodiments, a frustule can include a plurality of nanostructures on at least one surface, where the plurality of nanostructures includes an oxide of manganese, and where a ratio of a mass of the plurality of nanostructures to a mass of the frustule is about 1:1 to about 20:1. In some embodiments, the oxide of manganese includes MnO. In some embodiments, the oxide of manganese includes Mn_3O_4. In some embodiments, the oxide of manganese includes at least one of Mn_2O_3 and MnOOH. In some embodiments, the plurality of nanostructures includes at least one of nanowires, nanoplates, dense nanoparticles, nanobelts, and nanodisks. In some embodiments, the frustule includes a plurality of pores substantially not occluded by the plurality of nanostructures.

In some embodiments, an electrode of an energy storage device can include a plurality of frustules, where each of the plurality of frustules includes a plurality of nanostructures formed on at least one surface, where at least one of the plurality of frustules has a ratio of a mass of the plurality of nanostructures to a mass of the at least one frustule of about 1:20 to about 20:1.

In some embodiments, the electrode can include carbon nanotubes. In some embodiments, the electrode can include a conductive filler. The conductive filler may include graphite. In some embodiments, the electrode can include an ionic liquid.

In some embodiments, each of the plurality of frustules includes a plurality of pores substantially not occluded by the plurality of nanostructures.

The electrode may be an anode of the energy storage device. In some embodiments, the anode can include an electrolyte salt. In some embodiments, the electrolyte salt can include a zinc salt. In some embodiments, the plurality of nanostructures can include zinc oxide. In some embodiments, the plurality of nanostructures can include at least one of nanowires, nanoplates, dense nanoparticles, nanobelts, and nanodisks.

The electrode may be a cathode of the energy storage device. In some embodiments, the plurality of nanostructures can include an oxide of manganese. In some embodiments, the oxide of manganese can include MnO. In some embodiments, the oxide of manganese can include at least one of Mn_3O_4, Mn_2O_3 and MnOOH.

In some embodiments, an energy storage device can include a cathode having a first plurality of frustules, the first plurality of frustules having nanostructures including an oxide of manganese; and an anode having a second plurality of frustules, the second plurality of frustules having nanostructures including zinc oxide. In some embodiments, the device can be a rechargeable battery. In some embodiments, at least one of the first plurality of frustules includes a ratio of a mass of the oxide of manganese to a mass of the at least one frustule of about 1:20 to about 100:1. In some embodiments, at least one of the second plurality of frustules includes a ratio of a mass of the zinc oxide to a mass of the at least one frustule of about 1:20 to about 100:1.

In some embodiments, a frustule can include a plurality of nanostructures on at least one surface, where the plurality of nanostructures includes zinc oxide, and where a ratio of a mass of the plurality of nanostructures to a mass of the frustule is about 1:1 to about 100:1.

In some embodiments, a frustule can include a plurality of nanostructures on at least one surface, where the plurality of nanostructures includes an oxide of manganese, and where a ratio of a mass of the plurality of nanostructures to a mass of the frustule is about 1:1 to about 100:1.

In some embodiments, an electrode of an energy storage device can include a plurality of frustules, where each of the plurality of frustules includes a plurality of nanostructures formed on at least one surface, where at least one of the plurality of frustules has a ratio of a mass of the plurality of nanostructures to a mass of the at least one frustule of about 1:20 to about 100:1.

In some embodiments, a supercapacitor comprises a pair of electrodes and an electrolyte comprising an ionic liquid, wherein at least one of the electrodes comprises a plurality of frustules having formed thereon a surface active material.

In some embodiments, a supercapacitor comprises a pair of electrodes contacting an electrolyte, wherein at least one of the electrodes comprise a plurality of frustules and a zinc oxide.

In some embodiments, supercapacitor comprises a pair of electrodes contacting a non-aqueous electrolyte, wherein at least one of the electrodes comprise a plurality of frustules and a manganese oxide.

In some embodiments, a method of fabricating a supercapacitor comprises forming a separator between a pair of electrodes, wherein the separator comprises frustules, an electrolyte and a thermally conductive additive, wherein the thermally conductive additive is adapted to substantially absorb a near infrared (NIR) radiation upon being applied to the separator, thereby causing heating of the separator to accelerate drying.

For purposes of summarizing the invention and the advantages achieved over the prior art, certain objects and advantages are described herein. Of course, it is to be understood that not necessarily all such objects or advantages need to be achieved in accordance with any particular embodiment. Thus, for example, those skilled in the art will recognize that the invention may be embodied or carried out in a manner that can achieve or optimize one advantage or a group of advantages without necessarily achieving other objects or advantages.

All of these embodiments are intended to be within the scope of the invention herein disclosed. These and other embodiments will become readily apparent to those skilled in the art from the following detailed description having

reference to the attached figures, the invention not being limited to any particular disclosed embodiment(s).

BRIEF DESCRIPTION OF THE DRAWINGS

These and other features, aspects, and advantages of the present disclosure are described with reference to the drawings of certain embodiments, which are intended to illustrate certain embodiments and not to limit the invention.

FIG. **1** is a scanning electron microscope (SEM) image of diatomaceous earth comprising frustules.

FIG. **2** is a SEM image of an example frustule including a porous surface.

FIG. **3** is a SEM image of example frustules each having a substantially cylindrical shape.

FIGS. **4**A and **4**B are a flow diagram of example steps of a frustule separation process.

FIG. **5**A shows an example embodiment of a frustule comprising structures on both an exterior surface and an interior surface.

FIG. **5**B shows a SEM image, at 50 k× magnification, of an example frustule surface seeded with silver.

FIG. **5**C shows a SEM image, at 250 k× magnification, of a frustule surface seeded with silver.

FIG. **5**D shows a SEM image, at 20 k× magnification, of a frustule surface having silver nanostructures formed thereon.

FIG. **5**E shows a SEM image, at 150 k× magnification of a frustule surface having silver nanostructures formed thereon.

FIG. **5**F shows a SEM image, at 25 k× magnification, of a diatom frustule flake having a surface coated by silver nanostructures.

FIG. **5**G shows a SEM image, at 100 k× magnification, of a frustule surface seeded with zinc-oxide.

FIG. **5**H shows a SEM image, at 100 k× magnification, of a frustule surface seeded with zinc-oxide.

FIG. **5**I shows a SEM image, at 50 k× magnification, of a frustule surface having zinc-oxide nanowires formed thereon.

FIG. **5**J shows a SEM image, at 25 k× magnification, of a frustule surface having zinc-oxide nanowires formed thereon.

FIG. **5**K shows a SEM image, at 10 k× magnification, of a frustule surface having zinc-oxide nanoplates formed thereon.

FIG. **5**L shows a SEM image, at 50 k× magnification, of a frustule surface having silver nanostructures formed thereon.

FIG. **5**M shows a SEM image, at 10 k× magnification, of a frustule surface having zinc-oxide nanowires formed thereon.

FIG. **5**N shows a SEM image, at 100 k× magnification, of a frustule surface having zinc-oxide nanowires formed thereon.

FIG. **5**O shows a SEM image, at 500× magnification, of a plurality of frustules having zinc oxide nanostructures formed thereon.

FIG. **5**P shows a SEM image, at 5 k× magnification, of a frustule having zinc oxide nanostructures formed thereon.

FIG. **5**Q shows a SEM image, at 20 k× magnification, of a frustule surface having manganese oxide nanostructures formed thereon.

FIG. **5**R shows a SEM image, at 50 k× magnification, of a frustule surface having manganese oxide nanostructures formed thereon.

FIG. **5**S shows a TEM image of manganese oxide nanocrystals formed on a frustule surface.

FIG. **5**T shows an electron diffraction image of a manganese oxide particle.

FIG. **5**U shows a SEM image, at 10 k× magnification, of a frustule surface having manganese-containing nano-fibers formed thereon.

FIG. **5**V shows a SEM image, at 20 k× magnification, of a frustule having manganese oxide nanostructures formed thereon.

FIG. **5**W shows a SEM image, at 50 k× magnification, of a cross-section of an example frustule having manganese oxide nanostructures formed thereon.

FIG. **5**X shows a SEM image, at 100 k× magnification, of a frustule surface having manganese oxide nanostructures formed thereon.

FIG. **6** schematically illustrates an example embodiment of an energy storage device.

FIGS. **7**A through **7**E schematically illustrate examples of energy storage devices during various steps of different fabrication processes.

FIG. **8** shows an example embodiment of a separator for an energy storage device incorporating frustules in a separator layer.

FIG. **9** shows an example embodiment of an electrode for an energy storage device incorporating frustules in an electrode layer.

FIG. **10** shows a graph of a discharge curve of an example energy storage device.

FIG. **11** shows a graph of the cycling performance of the energy storage device of FIG. **10**.

FIG. **12** shows a graph of an example charge-discharge performance of an energy storage device.

FIG. **13** shows another graph of a charge-discharge performance of the energy storage device of FIG. **12**.

FIG. **14**A illustrates a cross-sectional view of a supercapacitor having both electrodes configured as a double-layer capacitor.

FIG. **14**B illustrates a cross-sectional view of the supercapacitor of FIG. **14**A in operation, where a voltage is applied across the electrodes.

FIG. **15** illustrates a cross-sectional view of a supercapacitor comprising an electrode that is configured as a pseudo capacitor.

FIGS. **16**A and **16**B illustrate experimental charge/discharge measurements performed on a supercapacitor having symmetric printed electrodes, where each of the electrodes having opposite polarities comprises frustules having formed thereon zinc oxide (Zn_xO_y) nano structures.

FIGS. **17**A-**17**D illustrate experimental charge/discharge measurements performed on a supercapacitor having symmetric printed electrodes, where each of the electrodes having opposite polarities comprises frustules having formed thereon manganese oxide (MnO_xO_y) nanostructures.

FIGS. **18**A-**18**E illustrate experimental charge/discharge measurements performed on a supercapacitor having asymmetric printed electrodes, where one of the electrodes having opposite polarities comprises frustules having formed thereon manganese oxide (MnO_xO_y) nanostructures, while the other of the electrodes comprises frustules having formed thereon CNT.

FIGS. **19**A-**19**B illustrate experimental charge/discharge measurements performed on a supercapacitor having symmetric printed electrodes, where each of the electrodes having opposite polarities comprises frustules having formed thereon CNT.

DETAILED DESCRIPTION

Although certain embodiments and examples are described below, those of skill in the art will appreciate that the invention extends beyond the specifically disclosed embodiments and/or uses and obvious modifications and equivalents thereof. Thus, it is intended that the scope of the invention herein disclosed should not be limited by any particular embodiments described below.

Energy storage devices used to power electronic devices generally include batteries (e.g., rechargeable batteries), capacitors, and super-capacitors (e.g., EDLCs, pseudo capacitors and hybrid supercapacitors). Energy storage devices may comprise an asymmetric energy storage device, including, for example, a battery-capacitor hybrid. Energy storage devices can be manufactured using printing technologies such as screen printing, roll-to-roll printing, ink-jet printing, etc. Printed energy storage devices can facilitate reduced energy storage device thickness, enabling compact energy storage. Printed energy storage devices can enable increased energy storage density by facilitating, for example, stacking of the energy storage devices. Increased energy storage density may facilitate use of printed energy storage devices for applications having a large power requirement, such as solar energy storage. Unlike energy storage devices having a rigid outer casing, printed energy storage devices may be implemented on a flexible substrate, enabling a flexible energy storage device. A flexible energy storage device can facilitate fabrication of flexible electronic devices, such as flexible electronic display media. Due to reduced thickness and/or flexible structure, printed energy storage devices may power cosmetic patches, medical diagnostic products, remote sensor arrays, smartcards, smart packaging, smart clothing, greeting cards, etc.

Reliability and durability of a printed energy storage device may be a factor hindering increased adoption of printed batteries. Printed energy storage devices typically lack a rigid outer casing, so printed energy storage devices may not stand up well to compressive pressure or shape deforming manipulation in use or production. Variation of an energy storage device layer thickness in response to compressive pressure or shape deforming manipulation may adversely affect device reliability. For example, some printed energy storage devices include electrodes spaced by a separator. Deviations in separator thickness may cause a short between the electrodes, such as when a separator is compressible and fails to maintain a separation between the electrodes under compressive pressure or shape deforming manipulation.

Costs associated with fabricating a printed energy storage device may also be a factor hampering use of printed energy storage devices to power a wider range of applications. Reliable fabrication of energy storage devices using printing technologies may facilitate cost-effective energy storage device production. Printing of an energy storage device may enable integrating the device printing process into the production of electronic devices, including for example printed electronic devices powered by the printed energy storage device, possibly enabling further cost savings. However, inadequate device structural robustness may hinder device integrity throughout the fabrication process, decreasing the feasibility of some printing technologies and impeding cost-effective production of the printed energy storage devices. Thickness of a printed energy storage device layer may also impede the use of certain printing technologies in the fabrication process, for example due to a device layer thickness that is greater than a film thickness at which the printing technology can effectively print.

As described herein, frustules may have significant mechanical strength or resistance to shear stress, for example due to dimensions, shape, porosity, and/or material. According to some implementations described herein, an energy storage device includes one or more components, for example one or more layers or membranes of a printed energy storage device, comprising frustules. An energy storage device comprising frustules may have mechanical strength and/or structural integrity such that the energy storage device is able to withstand compressive pressure and/or shape deforming manipulation, which can occur during manufacture or use, without failure, such that device reliability can increase. An energy storage device comprising frustules can resist variations in layer thicknesses, enabling maintenance of uniform or substantially uniform device layer thicknesses. For example, a separator comprising frustules may withstand compressive pressure or shape deforming manipulation to thereby facilitate improved energy storage device reliability by maintaining a uniform or substantially uniform separation distance between electrodes to inhibit or prevent a short in the device.

Increased mechanical strength in energy storage devices comprising frustules may facilitate reliable fabrication of the energy storage devices using various printing technologies, thereby enabling cost-effective device fabrication due to increased yield and/or integration of the fabrication process with the production process of applications powered by the devices.

Energy storage devices may be printed using an ink comprising frustules. For example, one or more membranes of a printed energy storage device may comprise frustules. One or more membranes of a printed energy storage device having frustules may be reliably printed onto a variety of substrates, including but not limited to, a flexible or inflexible substrate, a textile, a device, a plastic, any variety of films such as a metallic or semiconductor film, any variety of paper, combinations thereof, and/or the like. For example, suitable substrates may include graphite paper, graphene paper, polyester film (e.g., Mylar), polycarbonate film aluminum foil, copper foil, stainless steel foil, carbon foam, combinations thereof, and/or the like. Fabrication of printed energy storage devices on flexible substrates may allow for flexible printed energy storage devices that can be used in a wide array of devices and implementations due to increased reliability of certain such printed energy storage devices, for example due to increased robustness as a result of one or more layers comprising frustules.

Improved mechanical strength in printed energy storage devices comprising frustules may also enable a reduced printed device layer thickness. For example, frustules may provide structural support for an energy storage device layer, enabling thinner layers having sufficient structural robustness to withstand compressive pressure or shape deforming manipulation, which can then reduce an overall device thickness. Decreased thickness of printed energy storage devices can further facilitate energy storage density of the printed devices and/or enable wider use of the printed devices.

A printed energy storage device comprising frustules may have improved device performance, for example improved device efficiency. Reduced thickness of an energy storage device layer may enable improved device performance. Performance of an energy storage device may depend at least in part on the internal resistance of the energy storage device. For example, performance of an energy storage

device may depend at least in part on a separation distance between a first and a second electrode. A decreased separator membrane thickness for a given measure of reliability reduces a distance between a first and a second electrode, which can reduce the internal resistance and improve an efficiency of the energy storage device. Internal resistance of an energy storage device may also depend at least in part on the mobility of ionic species between a first and a second electrode. Porosity of frustule surfaces may enable mobility of ionic species. For example, a separator comprising frustules may enable a more structurally robust separation between electrodes of an energy storage device while facilitating mobility of ionic species between the electrodes. Frustule surface porosity may facilitate a direct path for mobile ionic species between a first electrode and a second electrode, reducing a resistance and/or increasing efficiency. Reduced thickness of an electrode layer comprising frustules and porosity of the electrode frustules may also enable improved storage device performance. A reduced electrode thickness may provide increased access of ionic species to active materials within the electrode. Porosity and/or conductivity of frustules in an electrode may facilitate mobility of the ionic species within the electrode. Frustules in an electrode may also enable improved device performance by, for example, serving as a substrate on which active materials and/or structures comprising active materials may be applied or formed, enabling increased surface area for active materials and thereby facilitating access of ionic species to the active materials.

FIG. **1** is a SEM image of diatomaceous earth comprising frustules **10**.

The frustules **10** have a generally cylindrical shape, although some frustules are broken or differently shaped. In some embodiments, the cylindrical frustules **10** have a diameter between about 3 μm and about 5 μm. In some embodiments, the cylindrical frustules **10** have a length between about 10 μm and about 20 μm. Other diameters and/or lengths are also possible. The frustules **10** may have significant mechanical strength or resistance to shear stress, for example due to architecture (e.g., dimensions, shape), material, combinations thereof, and/or the like. For example, mechanical strength of a frustule **10** may be inversely related to the size of the frustule **10**. In some embodiments, a frustule **10** having a longest axis in a range of from about 30 μm to about 130 μm can withstand compressive forces from about 90 μN to about 730 PT.

FIG. **2** is a SEM image of an example frustule **10** including a porous surface **12**. The porous surface **12** includes circular or substantially circular openings **14**. Other shapes of the openings **14** are also possible (e.g., curved, polygonal, elongate, etc.). In some embodiments, the porous surface **12** of a frustule **10** has a uniform or substantially uniform porosity, for example including openings **14** having uniform or substantially uniform shape, dimensions, and/or spacing (e.g., as shown in FIG. **2**). In some embodiments, the porous surface **12** of a frustule **10** has a varying porosity, for example including openings **14** having different shapes, dimensions, and/or spacing. The porous surfaces **12** of a plurality of frustules **10** can have uniform or substantially uniform porosities, or porosity of the porous surfaces **12** of different frustules **10** may vary. A porous surface **12** may comprise nanoporosity, including for example microporosity, mesoporosity, and/or macroporosity.

FIG. **3** is a SEM image of example frustules **10** each having a cylindrical or substantially cylindrical shape. Frustule features may differ among different species of diatoms, each diatom species having frustules of a different shape, size, porosity, material, and/or another frustule attribute. Diatomaceous earth, which may be commercially available (e.g., from Mount Sylvia Diatomite Pty Ltd of Canberra, Australia, Continental Chemical USA of Fort Lauderdale, Fla., Lintech International LLC of Macon, Ga., etc.), can serve as a source of frustules. In some embodiments, diatomaceous earth is sorted according to a pre-determined frustule feature. For example, sorting may result in frustules each including a predetermined feature, such as shape, dimensions, material, porosity, combinations thereof, and/or the like. Sorting frustules may include one or a variety of separation processes such as, for example, filtering, screening (e.g., use of vibrating sieves for separation according to a frustule shape or size), a separation process involving voraxial or centrifugal technology (e.g., for separation according to frustule density), any other suitable solid-solid separation processes, combinations thereof, and/or the like. Frustules may also be available (e.g., from a commercial source) already sorted according to a frustule feature such that the frustules already comprise a uniform or substantially uniform shape, size, material, porosity, another pre-determined frustule attribute, combinations thereof, and/or the like. For example, frustules available from a geographic region (e.g., a region of a country such as the United States, Peru, Australia, etc.; a region of the globe; etc.) and/or a type of natural environment (e.g., freshwater environment, saltwater environment, etc.) may comprise frustules of a species typically found in that geographic region and/or environment, providing frustules having a uniform or substantially uniform shape, size, material, porosity, another pre-determined frustule attribute, combinations thereof, and/or the like.

In some embodiments, a separation process can be used to sort frustules such that only or substantially only unbroken frustules are retained. In some embodiments, the separation process can be used to remove broken or small frustules, resulting in only or substantially only cylindrically-shaped frustules **10** having certain lengths and/or diameters (e.g., as illustrated in FIG. **3**). The separation process to remove broken frustules may include screening, such as with the use of a sieve having a mesh size selected to retain only or substantially only frustules having a pre-determined dimension. For example, the mesh size of the sieve may be selected to remove frustules having a dimension (e.g., a length or diameter) of no more than about 40 μm, no more than about 30 μm, no more than about 20 μm or no more than about 10 μm, and including ranges bordering and including the foregoing values. Other sieve mesh sizes may also be suitable.

In some embodiments, the separation process to remove broken frustules includes application of ultrasonic waves to frustules placed in a fluid dispersion, including for example ultrasonication during which frustules dispersed in a water bath are subjected to ultrasonic waves. Sonication parameters such as power, frequency, duration, and/or the like may be adjusted based at least in part on one or more attributes of the frustules. In some embodiments, ultrasonication includes use of sound waves having a frequency between about 20 kilohertz (kHz) and about 100 kHz, between about 30 kHz and about 80 kHz, and between about 40 kHz and about 60 kHz. In some embodiments, ultrasonication may use sound waves having a frequency of about 20 kHz, about 25 kHz, about 30 kHz, about 35 kHz, about 40 kHz, about 45 kHz, and ranges bordering and including the foregoing values. The ultrasonication step may have a duration between about 2 minutes and about 20 minutes, between about 2 minutes and about 15 minutes, and between about 5

minutes and about 10 minutes. In some embodiments, ultrasonication step may have a duration of about 2 minutes, about 5 minutes, about 10 minutes, and ranges bordering and including the foregoing values. For example, a frustule-fluid sample may be subjected to ultrasonic waves at a frequency of about 35 kHz for a duration of about 5 minutes.

In some embodiments, separation process includes sedimentation. For example, the separation process may include both ultrasonication and sedimentation such that heavier particles from the frustule-fluid sample may be allowed to settle out from the suspended phase of the frustule-fluid sample during ultrasonication. In some embodiments, the sedimentation process of heavier particles from the frustule-fluid sample has a duration between about 15 seconds and about 120 seconds, between about 20 seconds and about 80 seconds, and between about 30 seconds and about 60 seconds. In some embodiments, sedimentation has a duration of no more than about 120 seconds, no more than about 60 seconds, no more than about 45 seconds, no more than or about 30 seconds.

The separation process to remove broken frustules may include use of high-velocity centrifugal technology for physical separation based on density, including for example an ultracentrifugation step. For example, the separation process may include ultracentrifugation of the suspended phase of a frustule-fluid sample. Ultracentrifugation parameters such as angular velocity, duration, and/or the like may depend at least in part on the composition of the suspended phase (e.g., a density of the frustules) and/or characteristics of the equipment used. For example, the suspended phase may be ultracentrifuged at an angular velocity between about 10,000 rotations per minute (RPM) and about 40,000 RPM, between about 10,000 RPM and about 30,000 RPM, between about 10,000 RPM and about 20,000 RPM, and between about 10,000 RPM and about 15,000 RPM. The suspended phase may be ultracentrifuged for a duration between about 1 minute and about 5 minutes, between about 1 minute and about 3 minutes, and between about 1 minute and about 2 minutes. For example, the suspended phase of the frustule-fluid sample may be ultracentrifuged at an angular velocity of about 13,000 RPM for about 1 minute.

FIGS. **4**A and **4**B are a flow diagram of example steps of a frustule separation process **20**. The process **20** may enable separation of broken and/or unbroken diatom frustules from a solid mixture comprising, for example, broken and unbroken diatom frustules. In some embodiments, the separation process **20** enables large scale frustule sorting.

As described herein, there can be two sources of diatom frustules for nanostructured materials and/or nanodevices: living diatoms and diatomaceous earth. Diatoms can be taken directly from nature or cultured. Artificially, a large number of identical silica frustules can be cultured within a few days. To use natural diatoms for nanostructured materials and/or nanodevices, a separation process can be performed to separate the diatoms from other organic materials and/or substances. Another approach is to use diatomaceous earth. The sediments are abundant and the material is of low cost.

Diatomaceous earth can have frustules ranging from mixtures of different diatom species to a single diatom species (e.g., including some freshwater sediments). Diatomaceous earth can comprise broken and/or whole diatom frustules plus contaminating materials of different origin. Depending on application, one may use only whole diatom frustules, only broken frustules, or a mixture of both. For example, when separating whole frustules, diatomaceous earth with one kind of frustules may be used.

In some embodiments, a method of separating comprises separating whole diatom frustules from broken pieces of diatom frustules. In some embodiments, the separation process comprises sorting whole diatom frustules according to a common frustule characteristic (e.g., a dimension including a length or diameter, a shape, and/or a material) and/or sorting portions of diatom frustules based on a common frustule characteristic (e.g., a dimension including a length or diameter, a shape, degree of brokenness, and/or a material). For example, the separation process may enable extracting a plurality of diatom frustules or portions of diatom frustules having at least one common characteristic. In some embodiments, the separation process comprises removing contaminative material having a different chemical origin from the diatom frustules and/or portions of diatom frustules.

Diatoms and diatom frustules that stay unchanged during long time periods are sometimes used in biological, ecological, and related earth science research. Many approaches have been developed to extract small samples of frustules from water or sediments. The sediments (diatomaceous earth) contain diatom frustules (broken and unbroken) alongside with carbonates, mica, clay, organics and other sedimentary particles. The separation of unbroken frustules may involve three main steps: removal of organic remains, removal of particles with different chemical origin, and removal of broken pieces. The removal of organic matter may be realized with heating of samples in a bleach (e.g., hydrogen peroxide and/or nitric acid), and/or annealing at higher temperatures. The carbonates, clay, and other soluble non-silica materials may be removed by hydrochloric and/or sulfuric acid. For the separation of broken and unbroken frustules, several techniques can be applied: sieving, sedimentation and centrifugation, centrifugation with a heavy liquid, and split-flow lateral-transport thin separation cells, and combinations thereof. A problem for all of these approaches may often be aggregation of broken and unbroken frustules, which can diminish the quality of the separation, and/or may render the separation process suitable only for laboratory size samples.

Scaling up separation procedures may enable diatom frustules to be used as industrial nanomaterials.

In some embodiments, a separation procedure that can be utilized for industrial scale separation of diatoms comprises separation of diatom frustule portions having at least one common characteristic. For example, the common characteristic could be unbroken diatom frustules or broken diatom frustules. The separation process **20**, as shown in FIGS. **4**A and **4**B, is an example separation procedure enabling industrial scale separation of diatoms. In some embodiments, a separation procedure that enables large scale separation of diatoms enables a reduction in the agglomeration of frustules, such as by using a surfactant and/or a disc stack centrifuge. In some embodiments, use of the surfactant can enable the large scale separation. In some embodiments, using the disc stack centrifuge (e.g., a milk separator type centrifugation process) can enable large scale separation. For example, use of the surfactant to disperse diatom frustules together with a disc stack centrifuge to sort frustules based on a frustule characteristic may facilitate large scale separation of diatoms by enabling reduced agglomeration of the diatom frustules. A traditional, non-disk stack centrifuge process would cause sedimentation of the frustules. The supernatant fluid would be discarded, and the sedimented frustules would be redispersed in a solvent, after which the centrifuge would again cause sedimentation of the frustules. This process would be repeated until the desired separation

is achieved. A disk stack centrifuge process can continuously redisperse and separate sedimented frustules. For example, a phase enriched with whole diatoms can be continuously circulated through the disk stack centrifuge, becoming more and more enriched. In some embodiments, the disc stack centrifuge can enable a separation of broken diatom frustules from unbroken diatom frustules. In some embodiments, the disc stack centrifuge can enable a sorting of the diatom frustules according to a diatom frustule characteristic. For example, the disc stack centrifuge may enable extraction of frustules having at least one common characteristic (e.g., a dimension, a shape, a degree of brokenness and/or a material).

A separation procedure enabling industrial scale separation of diatoms, such as the separation process **20** shown in FIGS. **4**A and **4**B, may include the following steps:

1. Particles of a solid mixture (e.g., diatomaceous earth) comprising the diatom frustules and/or portions of diatom frustules may be rocky and can be broken down into smaller particles. For example, a particle size of the solid mixture may be reduced to facilitate the separation process **20**. In some embodiments, to obtain a powder, the diatomaceous earth can be mildly milled or ground, for example using a mortar and pestle, a jar mill, a rock crusher, combinations thereof, and/or the like.

2. In some embodiments, components of the diatomaceous earth that are larger than the diatom frustules or portions of diatom frustules may be removed through a sieving step. In some embodiments, the sieving step is performed after the diatomaceous earth has been milled. For example, diatomaceous earth powder may be sieved to remove the particles of the powder which are bigger than the frustules. In some embodiments, the sieving can be facilitated by dispersing the solid mixture (e.g., milled diatomaceous earth) in a liquid solvent. The solvent may be water, and/or other suitable liquid solvents. Dispersing the solid mixture in the solvent may be facilitated by sonicating the mixture comprising the solid mixture and the solvent. Other methods of aiding dispersion may also be suitable. In some embodiments, the dispersion comprises a weight percent of diatoms within a range of from about 1 weight percent to about 5 weight percent, about 1 weight percent to about 10 weight percent, about 1 weight percent to about 15 weight percent, or about 1 weight percent to about 20 weight percent. A concentration of the solid mixture in the dispersion may be reduced to facilitate the sieving step to remove particles of the dispersion that are larger than the diatoms. The sieve openings depend on the size of diatoms in the sample. For example, a suitable sieve may comprise a mesh size of about 20 microns, or any other mesh size that enables removal from the dispersion particles of the solid mixture that are larger than the diatoms (e.g., a sieve having a mesh size of about 15 microns to about 25 microns, or of about 10 microns to about 25 microns). A shaker sieve may be used for effectively increasing flow through the sieve.

3. In some embodiments, the separation process includes a purification step to remove organic contaminants from the diatoms (e.g., diatom frustules or portions of diatom frustules). A suitable process for removing organic contaminants may comprise immersing and/or heating the diatoms in a bleach (e.g., nitric acid and/or hydrogen peroxide), and/or annealing the diatoms at higher temperatures. For example, a sample of diatoms may be heated in a volume of a solution comprising about 10 volume percent to about 50 volume percent (e.g., 30 volume percent) hydrogen peroxide for about 1 minute to about 15 minutes (e.g., 10 minutes). Other compositions, concentrations and/or durations may be suitable. For example, the composition of the solution used, the concentration of the solution used, and/or the duration of the heating may depend on the composition of the sample to be purified (e.g., types of organic contaminants and/or diatoms). In some embodiments, the diatoms can be heated in a solution until the solution ceases or substantially ceases to bubble (e.g., indicating removal of organic contaminants is complete or substantially complete) to facilitate sufficient removal of the organic contaminants. Immersing and/or heating diatoms in a solution may be repeated until organic contaminants have been removed or substantially removed.

Purification of diatoms from organic contaminants may be followed by washing with water. In some embodiments, the diatoms may be washed with a liquid solvent (e.g., water). The diatoms may be separated from the solvent through a sedimentation process, including for example a centrifuge step. Suitable centrifuge technology may include, for example, a disc stack centrifuge, a decanter centrifuge, a tubular bowl centrifuge, combinations thereof, and/or the like.

4. In some embodiments, the separation process includes a purification step to remove inorganic contaminants. Inorganic contaminants may be removed by mixing the diatoms with hydrochloric and/or sulfuric acid. Inorganic contaminants may include carbonates, clay, and other soluble non-silica materials. For example, a sample of diatoms may be mixed with a volume of solution comprising about 15 volume percent to about 25 volume percent of hydrochloric acid (e.g., about 20 volume percent hydrochloric acid) for a duration of about 20 minutes to about 40 minutes (e.g., about 30 minutes). Other compositions, concentrations and/or durations may be suitable. For example, the composition of the solution used, the concentration of the solution used, and/or the duration of the mixing may depend on the composition of the sample to be purified (e.g., types of inorganic contaminants and/or diatoms). In some embodiments, the diatoms can be mixed in a solution until the solution ceases or substantially ceases to bubble (e.g., indicating removal of inorganic contaminants is complete or substantially complete) to facilitate sufficient removal of the inorganic contaminants. Mixing diatoms with a solution may be repeated until inorganic contaminants have been removed or substantially removed.

Purification of diatoms from soluble inorganic contaminants may be followed by washing with water. In some embodiments, the diatoms may be washed with a liquid solvent (e.g., water). The diatoms may be separated from the solvent through a sedimentation process, including for example a centrifuge step. Suitable centrifuge technology may include, for example, a disc stack centrifuge, a decanter centrifuge, a tubular bowl centrifuge, combinations thereof, and/or the like.

5. In some embodiments, the separation process comprises dispersing of frustules in a surfactant. The surfactant may facilitate separation of the frustules and/or portions of frustules from one another, reducing agglomeration of the frustules and/or portions of frustules. In some embodiments, an additive is used to reduce agglomeration of the diatoms. For example, diatoms may be dispersed in a surfactant and an additive. In some embodiments, dispersing of the diatoms in the surfactant and/or additive may be facilitated by sonicating the mixture comprising diatoms, the surfactant and/or the additive.

6. In some embodiments, broken frustule pieces may be extracted by a wet sieving process. For example, a filtering process may be used. In some embodiments, the filtering process comprises using a sieve for removing the smaller

pieces of broken frustules. The sieve may comprise a mesh size suitable for removing the smaller pieces of broken frustules (e.g., a 7 micron sieve). The wet sieving process can inhibit or prevent small sediment from accumulating in the pores of the sieve and/or allow small particles to pass through the pores of the sieve, for example by disturbing agglomeration of the sediment. Disturbing agglomeration may include, for example, stirring, bubbling, shaking, combinations thereof, and the like of materials which sediment on the sieve mesh. In some embodiments, the filtering process can be continuous through a series of sieves (e.g., having increasingly smaller pores or mesh sizes) (e.g., multiple sieves in a machine having a single input and output).

7. In some embodiments, a continuous centrifugation (milk separator-type machine) of frustules in a liquid can be used. For example, a disc stack centrifuge may be used. This process may be used to separate the diatoms according to a common characteristic, including for example, further separating broken frustule pieces from the unbroken frustules. In some embodiments, disc stack centrifuge step can be repeated to achieve a desired separation (e.g., desired level of separation of the broken frustules from the unbroken frustules).

8. As described herein, frustules may be washed in solvent, followed by a sedimentation process (e.g. centrifugation) in order to extract the frustules from the solvent. For example, centrifugation can be used to sediment frustules or portions of frustules after each washing step and/or before final use. Suitable centrifuge technology for sedimenting frustules after a wash step may include continuous centrifuges, including but not limited to a disc stack centrifuge, a decanter centrifuge, and/or a tubular bowl centrifuge.

The example separation procedure has been tested with fresh water diatoms from Mount Silvia Pty, Ltd. Diatomite mining company, Queensland, Australia. The majority of frustules in the sample has one kind of diatoms Aulacoseira sp. The frustules have cylindrical shape with diameter of about 5 microns and length from 10 to 20 microns.

Flow-chart of an example separation procedure, separation process **20** presented in FIGS. **4**A and **4**B only serves as an example. The quantities of parameters in the flowchart are provided as illustrative examples (e.g., suited to the chosen sample only). For example, quantities may be different for different types of diatoms.

The surface of diatoms can include amorphous silica and can include silanol groups, which are negatively charged. Isoelectric point found from zeta potential measurements can often be around pH2 for diatoms (e.g., similar to that of amorphous silica).

In some embodiments, the surfactant can comprise a cationic surfactant. Suitable cationic surfactants can include benzalkonium chloride, cetrimonium bromide, lauryl methyl gluceth-10 hydroxypropyl dimonium chloride, benzethonium chloride, benzethonium chloride, bronidox, dimethyldioctadecylammonium chloride, tetramethylammonium hydroxide, mixtures thereof, and/or the like. The surfactant may be a nonionic surfactant. Suitable nonionic surfactants can include: cetyl alcohol, stearyl alcohol, and cetostearyl alcohol, oleyl alcohol, polyoxyethylene glycol alkyl ethers, octaethylene glycol monododecyl ether, glucoside alkyl ethers, decyl glucoside, polyoxyethylene glycol octylphenol ethers, Triton X-100, Nonoxynol-9, glyceryl laurate, polysorbate, poloxamers, mixtures thereof, and/or the like.

In some embodiments, one or more additives can be added to reduce agglomeration. Suitable additives may include: potassium chloride, ammonium chloride, ammonium hydroxide, sodium hydroxide, mixtures thereof, and/or the like.

Frustules may have one or more modifications applied to a surface of the frustules. In some embodiments, frustules may be used as a substrate to form one or more structures on one or more surfaces of the frustules. FIG. **5**A shows an example frustule **50** comprising structures **52**. For example, a frustule **50** may have a hollow cylindrical or substantially cylindrical shape, and may comprise structures **52** on both an exterior and interior surface of the cylinder. The structures **52** may modify or affect a characteristic or attribute of the frustule **50**, including, for example, the conductivity of the frustule **50**. For example, an electrically insulating frustule **50** may be made electrically conductive by forming electrically conductive structures **52** on one or more surfaces of the frustule **50**. A frustule **50** may include structures **52** comprising silver, aluminum, tantalum, brass, copper, lithium, magnesium, combinations thereof, and/or the like. In some embodiments, a frustule **50** includes structures **52** comprising ZnO. In some embodiments, a frustule **50** includes structures **52** comprising an oxide of manganese, such as manganese dioxide (MnO_2), manganese (II, III) oxide (Mn_3O_4), manganese (II) oxide (MnO), manganese (III) oxide (Mn_2O_3), and/or manganese oxyhydroxide (MnOOH). In some embodiments, a frustule **50** includes structures **52** comprising other metal-containing compounds or oxides. In some embodiments, a frustule **50** includes structures **52** comprising a semiconductor material, including silicon, germanium, silicon germanium, gallium arsenide, combinations thereof, and/or the like. In some embodiments, frustules **50** comprise surface modifying structures **52** on all or substantially all of the surfaces of the frustules **50**.

Structures **52** applied or formed on a surface of a frustule **50** may comprise various shapes, dimensions, and/or other attributes. A frustule **50** may comprise structures **52** having a uniform or substantially uniform shape, dimension, and/or another structure **52** attribute. In some embodiments, a frustule **50** may have structures **52** comprising nanowires, nanotubes, nanosheets, nanoflakes, nanospheres, nanoparticles, structures having a rosette shape, combinations thereof, and/or the like. In some embodiments, a nanostructure can have a dimension having a length of about 0.1 nanometers (nm) to about 1000 nm. In some embodiments, the dimension is a diameter of the nanostructure. In some embodiments, the dimension is a longest dimension of the nanostructure. In some embodiments, the dimension is a length and/or width of the nanostructure. Nanostructures on surfaces of frustules may facilitate materials having increased surface area, advantageously providing materials having increased surface area on which electrochemical reaction can occur. In some embodiments, diatom frustules can reduce, prevent, or substantially prevent agglomeration of nanostructures in manufacturing processes and/or in products fabricated by the manufacturing processes (e.g., in an electrode fabricated using diatom frustules, devices comprising such an electrode). Reduction in agglomeration of nanostructures may facilitate providing increased active surface area for electrolyte to access (e.g., increase active surface area of an electrode, better electrical performance of a device comprising such an electrode). In some embodiments, the porosity of surfaces of diatom frustules can facilitate electrolyte access to the active surface area, such as facilitating diffusion of electrolytic ions to active surfaces of an electrode (e.g., diatom frustules can have pore sizes of about 1 nanometers (nm) to about 500 nm).

In some embodiments, the frustule **50** can be thickly covered by the nanostructures **52**. In some embodiments, a ratio of a mass of the nanostructures **52** to a mass of the frustule **50** is between about 1:1 and about 20:1, between about 5:1 and about 20:1, or between about 1:1 and about 10:1. The nanostructures **52** preferably have a mass greater than a mass of the frustule **50** prior to coating. The mass of the nanostructures **52** may be determined by weighing the frustules **50** before and after coating with the difference being the mass of the nanostructures **52**.

Structures **52** can be formed or deposited onto a surface of a frustule **50** at least in part by combining a frustule **50** with a formulation comprising a desired material to allow coating or seeding of the structures **52** onto a surface of the frustule **50**.

As described herein, structures **52** on a surface of the frustule **50** may comprise zinc oxide, such as zinc oxide nanowires. In some embodiments, zinc oxide nanowires can be formed on a surface of the frustule **50** by combining the frustule **50** with a solution comprising zinc acetate dihydrate ($Zn(CH_3CO_2)_2.2H_2O$) and ethanol. For example, a solution having a concentration of 0.005 mol/L (M) zinc acetate dihydrate in ethanol may be combined with frustules **50** so as to coat a surface of the frustules **50**. The coated frustules **50** may then be air dried and rinsed with ethanol. In some embodiments, the dried frustules **50** can then be annealed (e.g., at a temperature of about 350° C.). The zinc oxide nanowires may then be allowed to grow on the coated surface of the frustules **50**. In some embodiments, the annealed frustules **50** are maintained at a temperature above room temperature (e.g., maintained at around a temperature of about 95° C.) to facilitate formation of the zinc oxide nanowires.

Frustules **50** may also comprise a material formed on or deposited onto a surface of the frustules **50** to modify a characteristic or attribute of the frustules **50**. For example, an electrically insulating frustule **50** may be made electrically conductive by forming or applying an electrically conductive material on one or more surfaces of the frustule **50**. A frustule **50** may include a material comprising silver, aluminum, tantalum, brass, copper, lithium, magnesium, combinations thereof, and/or the like. In some embodiments, a frustule **50** includes material comprising ZnO. In some embodiments, a frustule **50** includes material comprising an oxide of manganese. In some embodiments, a frustule **50** includes a material comprising a semiconductor material, including silicon, germanium, silicon germanium, gallium arsenide, combinations thereof, and/or the like. The surface modifying material may be on an exterior surface and/or an interior surface of the frustules **50**. In some embodiments, frustules **50** comprise a surface modifying material on all or substantially all of the surfaces of the frustules **50**.

A material can be formed or deposited onto a surface of a frustule **50** in part through combining a frustule **50** with a formulation including a desired material to allow coating or seeding of the material onto a surface of the frustule **50**.

As described herein, a material may be deposited onto a surface of the frustule **50**. In some embodiments, the material comprises a conductive metal such as silver, aluminum, tantalum, copper, lithium, magnesium, and brass. In some embodiments, coating a surface of the frustule **50** with a material comprising silver includes, at least in part, combining the frustule **50** with a solution comprising ammonia (NH_3) and silver nitrate ($AgNO_3$). In some embodiments, the solution can be prepared in a process similar to a process often used in preparing Tollens' reagent. For example, preparation of the solution may comprise addition of ammonia to aqueous silver nitrate to form a precipitate, followed by further addition of ammonia until the precipitate dissolves. The solution may then be combined with the frustule **50**. As an example, 5 milliliters (mL) of ammonia may be added to 150 mL of aqueous silver nitrate while stirring such that a precipitate forms, followed by addition of another 5 mL of ammonia until the precipitate dissolves. A mixture may then be formed by combining the solution with 0.5 grams (g) of frustules **50** and an aqueous solution of glucose (e.g., 4 g of glucose dissolved in 10 mL of distilled water). The mixture may then be placed into a container immersed in a bath maintained at a temperature (e.g., a warm water bath maintained at a temperature of about 70° C.) so as to facilitate the coating of the frustules 50.

Growing Nanostructures on Diatom Frustules or Portions of Diatom Frustules

As described herein, diatomaceous earth is naturally occurring sediment from fossilized microscopic organisms called diatoms. The fossilized microorganisms comprise hard frustules made from highly structured silica with sizes often between about 1 micron and about 200 microns. Different species of diatoms have different 3D shapes and features, which vary from source to source.

Diatomaceous earth can include a highly porous, abrasive, and/or heat resistant material. Due to these properties, diatomaceous earth has found wide applications including filtering, liquid absorption, thermal isolation, as ceramic additive, mild abrasive, cleaning, food additive, cosmetics, etc.

Diatom frustules have attractive features for nanoscience and nanotechnology—they have naturally occurring nanostructures: nanopores, nanocavities and nanobumps (e.g., as shown in FIGS. **1** to **3**). The abundance of frustule shapes depending on the diatom species (e.g., more than 105) is another attractive property. Silicon dioxide, from which the diatom frustules are made, can be coated or replaced by a useful substance while preserving the diatom nanostructures. Diatom nanostructures may serve as a useful nanomaterial for many processes and devices: dye-sensitized solar cells, drug delivery, electroluminescent displays, anode for Li-ion batteries, gas sensors, biosensors, etc. Formation of MgO, ZrO_2, TiO_2, $BaTiO_3$, SiC, SiN, and Si may be accomplished using high temperature gas displacement of SiO_2.

In some embodiments, diatom frustules can be coated with 3D nanostructures. The diatoms may be coated on inner and/or outer surfaces, including inside the nanopores of the diatoms. The coatings may not preserve the diatom structure precisely. However, coatings may themselves have nanopores and nanobumps. Such silica frustules/nanostructures composites use frustules as support. The nanostructured material may have small nanoparticles densely joined together: nanowires, nanospheres, nanoplates, dense array of nanoparticles, nanodisks, and/or nanobelts. Overall, the composites may have a very high surface area.

Nanostructures comprising various materials may be formed on surfaces of frustules. In some embodiments, nanostructures comprise a metallic material. For example, nanostructures formed on one or more surfaces of a frustule may comprise zinc (Zn), magnesium (Mg), aluminum (Al), mercury (Hg), cadmium (Cd), lithium (Li), sodium (Na), calcium (Ca), iron (Fe), lead (Pb), nickel (Ni), silver (Ag), combinations thereof, and/or the like. In some embodiments, nanostructures comprise metal oxides. For example, nanostructures formed on a frustule surface may comprise zinc oxide (ZnO), manganese dioxide (MnO_2), manganese(II,

III) oxide (Mn_3O_4), manganese(II) oxide (MnO), manganese(III) oxide (Mn_2O_3), mercury oxide (HgO), cadmium oxide (CdO), silver (I,III) oxide (AgO), silver(I) oxide (Ag_2O), nickel oxide (NiO), lead(II) oxide (PbO), lead(II, IV) oxide (Pb_2O_3), lead dioxide (PbO_2), vanadium(V) oxide (V_2O_5), copper oxide (CuO), molybdenum trioxide (MoO_3), iron(III) oxide (Fe_2O_3), iron(II) oxide (FeO), iron(II, III) oxide (Fe_3O_4), rubidium(IV) oxide (RuO_2), titanium dioxide (TiO_2), iridium(IV) oxide (IrO_2), cobalt(II, III) oxide (Co_3O_4), tin dioxide (SnO_2), combinations thereof, and/or the like. In some embodiments, nanostructures comprise other metal-containing compounds, including for example, manganese(III) oxohydroxide (MnOOH), nickel oxyhydroxide (NiOOH), silver nickel oxide ($AgNiO_2$), lead(II) sulfide (PbS), silver lead oxide ($Ag_5Pb_2O_6$), bismuth(III) oxide (Bi_2O_3), silver bismuth oxide ($AgBiO_3$), silver vanadium oxide (AgV_2O_5), copper(I) sulfide (CuS), iron disulfide (FeS_2), iron sulfide (FeS), lead(II) iodide (PbI_2), nickel sulfide (Ni_3S_2), silver chloride (AgCl), silver chromium oxide or silver chromate (Ag_2CrO_4), copper(II) oxide phosphate ($Cu_4O(PO_4)_2$), lithium cobalt oxide ($LiCoO_2$), metal hydride alloys (e.g., LaCePrNdNiCoMnAl), lithium iron phosphate ($LiFePO_4$ or LFP), lithium permanganate ($LiMn_2O_4$), lithium manganese dioxide ($LiMnO_2$), Li(NiMnCo)O_2, Li(NiCoAl)O_2, cobalt oxyhydroxide (CoOOH), titanium nitride (TiN), combinations thereof, and/or the like.

In some embodiments, nanostructures formed on surfaces of frustules can comprise non-metallic or organic material. In some embodiments, the nanostructures can comprise carbon. For example, the nanostructures may comprise multi-wall and/or single-wall carbon nanotubes, graphene, graphite, carbon nano-onions, combinations thereof, and/or the like. In some embodiments, nanostructures may comprise fluorocarbons (e.g., CF_x), sulfur (S), conductive n/p-type doped polymers (e.g., conductive n/p-type doped poly (fluorene)s, polyphenylenes, polypyrenes, polyazulenes, polynaphthalenes, poly(pyrrole)s, polycarbazoles, polyindoles, polyazepines, polyanilines, poly(thiophene)s, poly(3, 4-ethylenedioxythiophene), and/or poly(p-phenylene sulfide)), combinations thereof, and/or the like.

Nanostructures formed on a surface of a diatom frustule may include: 1) silver (Ag) nanostructures; 2) zinc-oxide (ZnO) nanostructures; 3) carbon nanotubes "forest;" and/or 4) manganese-containing nanostructures. As described herein, the diatom frustules having nanostructures formed on one or more of their surfaces can be used for energy storage devices such as batteries and supercapacitors, solar cells, and/or gas sensors. Nanostructures may be formed on one or more surfaces of unbroken frustules and/or broken frustules. In some embodiments, frustules or portions of frustules used in the nanostructure formation process may have been extracted through a separation procedures comprising separation steps described herein (e.g., the separation process **20** shown in FIGS. **4**A and **4**B). In some embodiments, before the growth of nanostructured active materials, frustules can be pretreated with one or more functionalized chemicals (e.g., siloxanes, fluorosiloxanes, proteins, and/or surfactants). In some embodiments, before the growth of nanostructured active materials, frustules can be pre-coated with a conductive materials (e.g., metal, and/or a conductive carbon), and/or a semiconductor material. For example, frustules may be pre-coated with silver (Ag), gold (Au), copper (Cu), nickel (Ni), platinum (Pt), graphene, graphite, carbon nanotubes, silicon (Si), germanium (Ge)), a semiconductor-containing alloy (e.g., an aluminum-silicon (AlSi) alloy), combinations thereof, and/or the like.

In some embodiments, nanostructures are grown using two step approaches. The first step generally includes the growth of seeds on the surface of diatom frustules. Seeds are nanostructures that are directly bonded (e.g., chemically bonded) to the surfaces of the diatom frustules, and may have certain grain size and/or uniformity. Energy may be provided to create such bonds. The seeding process may be conducted under high temperatures and/or involve other techniques that can create heat or some other form of energy gain.

A second step of forming nanostructures generally includes growing the final nanostructures from the seeds. Frustules pre-coated with seeds may be immersed in environments of initial materials under certain conditions. The nanostructures may include one or more of nanowires, nanoplates, dense nanoparticles, nanobelts, nanodisks, combinations thereof, and/or the like. The form factor may depend on conditions of the growth of the nanostructures (e.g., morphology of the nanostructures can depend on one or more growth conditions during forming of the nanostructures on the seed layer, including for example a growth temperature, a pattern of heating, inclusion of a chemical additive during the nanostructure growth, and/or combinations thereof).

An Example Process of Forming Ag Nanostructures on Surfaces of Diatom Frustules

The initial coating of silica with silver (or seeding) can be realized by reduction of a Ag^+ salt using microwave, ultrasonication, surface modification, and/or reduction of silver nitrate ($AgNO_3$) with a reducing agent.

The seed growth step may include dissolution of a silver salt and a reducing agent in a solvent (e.g., the reducing agent and the solvent can be the same substance) and dispersing purified diatoms in the mixture. During and/or after the dissolution, a physical force like mixing, stirring, heating, ultrasonication, microwaves, combinations thereof, and/or the like may be applied. The seed layer growth process may occur for various amounts of time.

Examples of Growing Ag Seeds on Surfaces of Diatom Frustules

Example 1 includes the following steps: 0.234 g of purified diatoms, 0.1 g $AgNO_3$, and 50 mL of molten at 60° C. PEG 600 (polyethylene glycol) are mixed in a beaker. In some embodiments, a mixture comprising clean diatoms, a silver contributing component (e.g., silver nitrate), and a reducing agent may be heated by a cyclic heating regimen. In some embodiments, the reducing agent and the solvent can be the same substance. For example, a mixture may be heated for about 20 minutes to about 40, alternating the heat from about 100 Watt to about 500 Watt every minute. For example, the mixture comprising cleaned diatoms, silver nitrate, and molten PEG was heated by microwave for about 30 min. The microwave power was altered from 100 to 500 Watt every minute to prevent overheating the mixture. Some commercial microwaves allow the user to determine the temperature of the contents after a certain duration, and/or to determine multiple temperatures after various durations (e.g., to define a temperature ramp), during which the microwave controls the power in order to achieve that result. For example, the microwave may determine that a lower power is needed to heat 50 mL of water to 85° C. in 2 min than to heat 50 mL of water to 85° C. in 1 min, and this adjustment may be made during the heating process, for example based on temperature sensors. For another example, the microwave may determine that a lower power is needed to heat 50 mL of water to 85° C. in 2 min than to heat 100 mL of water to 85° C. in 2 min, and this adjustment

may be made during the heating process, for example based on temperature sensors. The diatoms were centrifuged and washed with ethanol. The seeds are illustrated in FIGS. **5**B and **5**C.

Example 2 includes the following steps: Mix 45 mL of N,N-dimethylformamide, 0.194 g of 6,000 MW PVP (polyvinylpyrrolidone), 5 mL of 0.8 mM $AgNO_3$ in water, and 0.1 g of filtered and purified diatoms in a beaker. A tip of an ultrasonic processor (e.g., 13 mm diameter, 20 kHz, 500 Watt) is placed in the mixture and the beaker with the mixture placed in an ice bath. Tip amplitude is set at 100%. Sonication lasts 30 min. The diatoms are cleaned after the procedure in ethanol two times using bath sonication and centrifugation at 3,000 RPM for 5 min. Then the process is repeated two more times until seeds are seen on the diatoms.

FIG. **5**B shows a SEM image, at 50 k× magnification, of silver seeds **62** formed on a surface of a diatom frustule **60**. FIG. **5**C shows a SEM image, at 250 k× magnification, of the silver seeds **62** formed on the surface of the diatom frustule **60**.

Example of Forming Silver Nanostructures on Silver Seeded Diatom Frustule Surfaces

Further coating of the seeded frustules with silver may be conducted under argon (Ar) atmosphere to inhibit formation of silver oxides. In some embodiments, diatom frustule portions can be sintered (e.g., heated to a temperature of about 400° C. to about 500° C.) to obtain silver from silver oxides which may have formed on one or more surfaces of diatom frustule portions, including silver oxides formed during the process to further coat the seeded diatom frustule portions with silver. For example, sintering of diatom frustule portions may be performed on diatom frustule portions used in fabricating a conductive silver ink (e.g., a UV-curable conductive silver ink as described herein). In some embodiments, the sintering may be under an atmosphere configured to promote reduction of silver oxides to silver (e.g., hydrogen gas). Sintering the diatom frustule portions that the conductive silver ink comprises to obtain silver from silver oxides may improve conductivity of the conductive silver ink, for example because silver is more conductive than silver oxide and/or because silver-silver contact (e.g., as opposed to silver-silver oxide contact and/or silver oxide-silver oxide contact) may be increased. Other methods of obtaining silver from silver oxide may also be suitable in place of or in combination with sintering, including, for example, a process comprising a chemical reaction.

Formation of nanostructures on the seed layer may include a silver salt, a reducing agent, and a solvent. A mixing step, a heating step, and/or a titration step (e.g., to facilitate interaction of components of the nanostructure growth process) may be applied to form the nanostructures on the seed layer.

An example of process for forming the nanostructures on the seed layer (e.g., forming a thick silver coating) includes the following process:

5 mL of 0.0375 M PVP (6,000 MW) solution in water is placed in one syringe and 5 mL of 0.094 M $AgNO_3$ solution in water is placed in another syringe. 0.02 g of seeded washed and dried diatoms mixed with 5 mL of ethylene glycol heated to about 140° C. The diatoms are titrated with silver salt (e.g., $AgNO_3$) and PVP solutions at a rate of about 0.1 milliliter per minute (mL/min) using a syringe pump. After the titration is finished, the mixture is stirred for about 30 min. Then diatoms are washed (e.g., washed two times) using ethanol, bath sonication, and centrifugation.

FIGS. **5**D and **5**E show SEM images of an example where silver nanostructures **64** have formed on a surface of diatom frustule **60**. FIGS. **5**D and **5**E show a frustule **60** having a thick nanostructured coating with high surface area. FIG. **5**D is a SEM image of the frustule surface at 20 k× magnification, while FIG. **5**E shows a SEM image of the frustule surface at 150 k times magnification. FIG. **5**L is another SEM image, at 50 k× magnification, of the diatom frustule **60** having silver nanostructures **64** on a surface. The thick nanostructured coating of diatom frustule **60** can be seen in FIG. **5**L.

Examples of suitable reducing agents for Ag growth include common reducing agents used for silver electroless deposition. Some suitable reducing agents for silver electroless deposition include hydrazine, formaldehyde, glucose, sodium tartrate, oxalic acid, formic acid, ascorbic acid, ethylene glycol, combinations thereof, and/or the like.

Examples of suitable Ag^+ salts and oxides include silver salts. The most commonly used silver salts are soluble in water (e.g., $AgNO_3$). Suitable silver salts may include an ammonium solution of $AgNO_3$ (e.g., $Ag(NH_3)_2NO_3$). In some embodiments, any silver (I) salt or oxide can be used (e.g., soluble and/or not soluble in water). For example, silver oxide (Ag_2O), silver chloride (AgCl), silver cyanide (AgCN), silver tetrafluoroborate, silver hexafluorophosphate, silver ethylsulphate, combinations thereof, and/or the like, may also be suitable.

Suitable solvents may include: water, alcohols such as methanol, ethanol, N-propanol (including 1-propanol, 2-propanol (isopropanol or IPA), 1-methoxy-2-propanol), butanol (including 1-butanol, 2-butanol (isobutanol)), pentanol (including 1-pentanol, 2-pentanol, 3-pentanol), hexanol (including 1-hexanol, 2-hexanol, 3-hexanol), octanol, N-octanol (including 1-octanol, 2-octanol, 3-octanol), tetrahydrofurfuryl alcohol (THFA), cyclohexanol, cyclopentanol, terpineol; lactones such as butyl lactone; ethers such as methyl ethyl ether, diethyl ether, ethyl propyl ether, and polyethers; ketones, including diketones and cyclic ketones, such as cyclohexanone, cyclopentanone, cycloheptanone, cyclooctanone, acetone, benzophenone, acetylacetone, acetophenone, cyclopropanone, isophorone, methyl ethyl ketone; esters such ethyl acetate, dimethyl adipate, propylene glycol monomethyl ether acetate, dimethyl glutarate, dimethyl succinate, glycerin acetate, carboxylates; carbonates such as propylene carbonate; polyols (or liquid polyols), glycerols and other polymeric polyols or glycols such as glycerin, diol, triol, tetraol, pentanol, ethylene glycols, diethylene glycols, polyethylene glycols, propylene glycols, dipropylene glycols, glycol ethers, glycol ether acetates 1,4-butanediol, 1,2-butanediol, 2,3-butanediol, 1,3-propanediol, 1,4-butanediol, 1,5-pentanediol, 1,8-octanediol, 1,2-propanediol, 1,3-butanediol, 1,2-pentanediol, etohexadiol, p-menthane-3,8-diol, 2-methyl-2,4-pentanediol; tetramethyl urea, n-methylpyrrolidone, acetonitrile, tetrahydrofuran (THF), dimethyl formamide (DMF), N-methyl formamide (NMF), dimethyl sulfoxide (DMSO); thionyl chloride; sulfuryl chloride, combinations thereof, and/or the like.

In some embodiments, a solvent can also act as a reducing agent.

Example Method of Fabricating a Low-Cost UV-Curable Silver-Diatom Conductive Ink

Thermally curable silver flake and silver nanoparticle conductive inks are available from a variety of manufacturers such as Henkel Corp., Spraylat Corp., Conductive Compounds, Inc., DuPont, Inc., Creative Materials Corp., et al. A much less common product is a silver conductive ink curable with ultraviolet (UV) light. Only a few suppliers, (e.g., Henkel Corp.) have such inks in their product offerings. UV-curable silver conductive inks often can be very

costly because of the high silver loading, and high cost per square meter relative to the conductivity. The conductivities can be as much as 5 to 10 times lower than thermally cured silver conductive inks applied at the same wet film thickness.

There is clearly a need for a low-cost UV-curable silver with at least the same or better conductivity than the currently available UV-curable inks. Some UV-curable silvers may not take full advantage of the volume of silver present in the ink, so there is a need to develop a silver ink using much less silver that has similar or better conductivity and/or curability than current UV-curable silver inks.

A difficulty with developing UV-curable silvers may be due to the UV absorption properties of silver. In thermally-cured silver inks, silver flakes having a high aspect ratio may be used to produce the highest conductivity by maximizing the inter-flake contact area. If this type of silver flake is mixed with a UV-curable resin system appropriate for a conductive ink, applied to a surface using printing or other coating processes, and then exposed to UV light, most of the UV light may be absorbed by the silver before the UV light can scatter through the wet layer of silver ink. UV absorption by silver flakes can impede or prevent UV light-initiated polymerization from occurring in the wet ink film (e.g., impeding or preventing UV light-initiated polymerization of the wet ink beyond a certain depth). Reduced polymerization of the ink film may result in an incompletely cured layer of silver ink that may not adhere to the substrate, for example due to the bottom-most portions of the silver ink layer being uncured and wet. Lower aspect-ratio silver particles may be used in UV-curable silver inks to obtain suitable curing throughout the applied layer of silver ink by increasing the number of possible light scattering paths through the applied layer of silver ink. The low aspect-ratio particles have decreased surface area, which may reduce inter-flake contact area, and in turn may reduce conductivity of the cured film relative to what would be possible if a high aspect-ratio flake was used. If this curing problem could be solved, larger aspect ratio silver flake with higher conductivity could be used in the silver ink, which may improve conductivity of the resulting silver film and/or reduce the amount of silver used to achieve a high conductivity.

In some embodiments, a non-conducting substrate (e.g., a diatom frustule portion, such a diatom frustule flake) can be plated with silver. UV light may pass through the perforations on one or more surfaces of the body of the diatom frustule flake. Using the silver plated diatom flake in the silver ink may facilitate curing of the silver ink, enabling the use of high aspect ratio flakes in the silver ink. In some embodiments, a silver ink comprising silver plated diatom frustules may enable increased conductivity of the cured silver ink while, at the same time, reducing the cost of the ink.

In some embodiments, the portions of diatom frustules (e.g., broken diatom frustules) used in the silver ink can be purified and separated from the intact diatom particles, and one or more surfaces of the portions of diatom frustules may be electrolessly coated with silver, for example according to methods described herein.

A diatom surface may be perforated by a regular pattern of holes or openings (e.g., including holes approximately 300 nm in diameter), even when coated with silver. The openings may be large enough to allow UV wavelengths to scatter through the silver coated diatom particles. Broken diatoms coated with silver may comprise shards in the form of high aspect-ratio perforated flakes. FIG. **5**F shows a SEM image of a broken piece of diatom frustule (e.g., a diatom frustule flake **60**A) coated with Ag nanostructures (e.g., silver nanostructures **64**).

In some embodiments, a silver coated perforated diatom flake can be used for making a UV-silver ink which can be cured when a moderately thickly ink is used (e.g., a silver ink having a thickness of about 5 μm to about 15 μm), even though the conductive particles have high aspect-ratios and therefore large surface areas. Large surface areas of the frustule flake may create excellent inter-flake conductivity by increasing the number of inter-flake electrical contacts, resulting in a highly conductive ink that uses substantially only as much silver as is needed to achieve the desired sheet conductivity, with the rest of the volume taken up by the inexpensive diatom filler material and UV binder resin.

The silver nanostructure may cover substantially all surfaces of the frustules, including the inner surfaces of the frustule perforations, but without blocking the perforations (e.g., one or more surfaces of the perforations and frustule surfaces may be plated with silver nanostructures and/or a silver seed layer). The perforations in the Ag coated diatom flakes may allow UV radiation to pass through the diatom flakes, facilitating curing to a deep depth within the applied silver ink films while allowing current to be conducted directly from one side of the flake to the other through the perforations. A reduction in the length of the conduction pathways through the flake may reduce the overall resistance of the cured film made from the silver ink.

An example UV light-induced polymerizable ink formulation may include components from the following list. In some embodiments, a silver ink having diatom frustule flakes can be fabricated by combining components listed below, including, for example, combining a plurality of frustule portions (e.g., frustule flakes) having silver nanostructures formed on one or more surfaces with one or more other silver ink components listed below. A silver film may be fabricated by curing the silver ink with a UV light source.

1) Diatoms, any of a variety of species, plated (e.g., having nanostructure formed thereon) with between about 10 nm and about 500 nm thick Ag coating. A thickness of the Ag coating may depend on a pore size of the diatom perforations. Ratios in the formulation may be between about 50% and about 80% by weight. An example diatom species whose fragments can be used is Aulacoseira sp. 1.

2) A polar vinyl monomer with good affinity for silver, such as n-vinyl-pyrrolidone or n-vinylcaprolactam.

3) An acrylate oligomer with good elongation properties as a rheology modifier and to improve flexibility in the cured film.

4) One or more difunctional or trifunctional acrylate monomers or oligomers as crosslinking agents to produce a tougher, more solvent resistant cured film through increased cross-linking. These materials may be chosen to function as photoinitiation synergists, which may improve surface curing. Examples may include ethoxylated or propoxylated hexandiol acrylates such as Sartomer CD560®, ethoxylated trimethylpropane triacrylate available, for example from Sartomer under the product code SR454®, or triallyl cyanurate available, for example from Sartomer under the product code SR507A®. Acrylated amine synergists may be an option, and examples may include Sartomer CN371® and Sartomer CN373®.

5) An acrylate-based flow and level agent to reduce bubbling and improve wet ink quality (e.g., suitable flow and level agents may include Modaflow 2100®, Modaflow 9200®). Improved wet ink quality may, in turn, improve cured silver ink film quality.

6) One or more photoinitiators appropriate for pigment loaded ink systems. In some embodiments, at least one of the photoinitiatiors is sensitive to wavelengths near to or smaller than the silver plated diatom flake's average pore size so that UV photons may pass through the pore in order to initiate polymerization underneath the flake and/or scatter through a perforation in another silver plated diatom flake to penetrate even deeper into the uncured film to initiate polymerization there. Examples of photoinitiators can include Ciba Irgacure 907® and Isopropyl thioxanthoone (ITX, available from Lambson, UK under the tradename Speedcure ITV)).

7) An optional adhesion promoting acrylate (e.g., 2-carboxyethyl acrylate).

8) A optional wetting agent to lower surface tension and improve flake wetting (e.g., DuPont Capstone FS-30® and DuPont Capstone FS-31®).

9) An optional UV stabilizer to suppress premature polymerization triggered by the presence of silver metal (e.g., hydroquinone and methyl ethyl hydroquinone (MEHQ)).

10) An optional low boiling point solvent for lowering viscosity to facilitate the silver ink formulation being used in high speed coating processes, including processes such flexographic printing, gravure printing, combinations thereof, and/or the like.

In some embodiments, a silver ink comprising diatom frustule portions can be thermally cured. In some embodiments, the silver ink can be exposed to a heat source. For example, the silver ink may be heated to facilitate a polymerization reaction between polymer components of the silver ink. In some embodiments, thermal curing of the silver ink can facilitate removal of a solvent component. For example, the silver ink can be exposed to a heat source to raise a temperature of the silver ink above a boiling point of the silver ink solvent component to facilitate removal of the solvent component.

Example Processes of Forming Zinc-Oxide (ZnO) Nanostructures on Surfaces of Diatom Frustules

Generally, the ZnO seeds on a substrate can be deposited using spray or spin coating of colloidal ZnO or with thermal decomposition of zinc salts solutions. For example, thermal decomposition of zinc acetate precursor can give vertically well-aligned ZnO nanowires.

Growth of ZnO nanostructures from seeds may be realized by the hydrolysis of Zn salts in a basic solution. The process can be performed at room temperature or at higher temperatures. Microwave heating can significantly accelerate growth of nanostructures. Depending on growth parameters, different nanostructures were observed (e.g., morphology of the nanostructures can depend on one or more growth conditions during forming of the nanostructures on the seed layer, including for example a growth temperature, a pattern of heating, inclusion of a chemical additive during the nanostructure growth, and/or combinations thereof). For example, a chemical additive may be used to achieve a desired morphology of nanostructures. ZnO nanostructures also can be doped to control their semiconducting properties.

Example Processes for Growing ZnO Seeds on Surfaces of Diatom Frustules

1. Building seeds of ZnO can be realized by heating a mixture of 0.1 g of purified diatoms and 10 mL of 0.005 M zinc acetate ($Zn(CH_3COO)_2$) (e.g., a zinc contributing component) in ethanol to about 200° C. (e.g., including from about 175° C. to about 225° C.) until dry. SEM images, each at 100 k× magnification, of a ZnO seeded frustule surface are shown in FIGS. **5**G and **5**H. FIGS. **5**G and **5**H show SEM images of seeds **72** comprising ZnO formed on a surface of a frustule **70**. FIG. **5**G shows a SEM image, at 100 k× magnification, of a frustule surface having seeds **72** comprising zinc-oxide. FIG. **5**H shows a SEM image, at 100 k× magnification, of a frustule surface having seeds **72** comprising zinc-oxide.

In some embodiments, a process of seeding frustule surfaces with ZnO comprises forming a mixture comprising the following composition: about 2 weight % to about 5 weight % frustules, about 0.1 weight % to about 0.5 weight % of zinc salt (e.g., $Zn(CH_3COO)_2$), and about 94.5 weight % to about 97.9 weight % of an alcohol (e.g., ethanol). In some embodiments, forming the ZnO seeds on the frustule surfaces comprises heating the mixture. The mixture may be heated to a desired temperature for a period of time to facilitate formation of ZnO seeds on surfaces of the frustules and removal of liquids from the mixture. Heating may be performed using any number of heating apparatuses capable of heating the mixture to the desired temperature for the desired period of time, such as a hot plate. In some embodiments, the mixture can be heated to a temperature of greater than about 80° C. to facilitate formation of ZnO seeds on the frustule surfaces and to dry the ZnO seeded frustules. In some embodiments, the heated mixture may be further heated in a vacuum oven to facilitate further removal of liquids. For example, the mixture may be heated in a vacuum oven at a pressure of about 1 millibar (mbar) and at a temperature of about 50° C. to about 100° C.

In some embodiments, the dried frustules can be subjected to an annealing process. In some embodiments, the annealing process can be configured to facilitate desired formation of ZnO, for example by facilitating decomposition of the zinc salt to form ZnO. In some embodiments, conditions of the annealing process can be configured to achieve further drying of the frustules, such as by evaporation of any remaining liquids from the frustules. In some embodiments, the annealing process can comprise heating the dried frustules in an inert atmosphere at a temperature of about 200° C. to about 500° C. In some embodiments, the annealing process can include heating in an atmosphere comprising argon gas (Ar) and/or nitrogen gas (N_2).

Example Processes for Growing ZnO Nanostructures on ZnO Seeded Surfaces of Diatom Frustules

2. As described herein, ZnO nanostructures can be grown on the ZnO seeds formed on frustule surfaces. In some embodiments, ZnO nanostructure growth can be conducted in mixture of 0.1 g seeded frustules with 10 mL of 0.025 M $ZnNO_3$ (e.g., a zinc contributing component) and 0.025 M hexamethylenetetramine solution (e.g., a basic solution) in water. The mixture can be heated to about 90° C. (e.g., including from about 80° C. to about 100° C.) for about two hours (e.g., including from about one hour to about three hours) on a stir plate, or by using a cyclic heating routine (e.g., microwave heating) for a duration of about 10 min (e.g., including for a duration of about 5 minutes to about 30 minutes) where the sample is heated by about 500 Watt of power (e.g., including from about 480 Watt to about 520 Watt) for about 2 min (e.g., including about 30 seconds to about 5 minutes, about 1 minute to about 5 minutes, about 5 minutes to about 20 minutes) and then heating can be turned off for about 1 min (e.g., including from about 30 seconds to about 5 minutes) before repeating the heating at 500 Watt. The resulting nanowires **74** on the inside and outside surfaces of a frustule **70** using the above-described process are shown in FIGS. **5**I and **5**J. FIG. **5**I shows a SEM image, at 50 k× magnification, of ZnO nanowires **74** formed on both inside surfaces and outside surfaces of a diatom

frustule **70**. In some embodiments, ZnO nanowires **74** can be formed on a portion of a surface on an interior of a diatom frustule **70**. For example, ZnO nanowires **74** may be formed on all or substantially all surfaces on an interior of a diatom frustule **70**. ZnO nanowires **74** may be formed on all or substantially all interior and exterior surfaces of a diatom frustule **70**. The drawings of this application provide proof that growth of nanostructures (e.g., ZnO nanowires) on diatom frustules is possible, including growth of nanostructures (e.g., ZnO nanowires) on the inside of diatom frustules. Coating all or substantially all sides of the diatom frustules with ZnO nanostructures may provide increased conductivity of a material (e.g., ink or a layer printed therefrom) comprising the ZnO nanostructure-coated diatom frustules (e.g., an increased bulk conductivity and/or sheet conductivity), for example in comparison to materials (e.g., ink or a layer printed therefrom) comprising ZnO nanostructures formed only on the outside of a substrate. FIG. **5**J shows a SEM image, at 25 k× magnification, of ZnO nanowires **74** formed on surfaces of a diatom frustule **70**. FIGS. **5**M and **5**N are additional SEM images of diatom frustule **70** having ZnO nanowires **74** on one or more surfaces. FIG. **5**M is a SEM image of diatom frustule **70** at 10 k× magnification. FIG. **5**N is a SEM image of diatom frustule **70** at 100 k× magnification. The polyhedral, polygonal cross-section, and rod-like structure of the ZnO nanowires **74** and their attachment to the surface of the frustule **70** can be more clearly seen in FIG. **5**N. When the heating was performed in a microwave at 100 Watt (e.g., including from about 80 Watt to about 120 Watt; and at about 2 min on, then about 1 min off, and repeated for a total duration of about 10 min), nanoplates **76** can be formed on a surface of the frustules **70** (e.g., as shown in FIG. **5**K).

In some embodiments, a process for forming ZnO nanostructures on one or more surfaces of frustules seeded with ZnO comprises forming a mixture comprising the following composition: about 1 weight % to about 5 weight % seeded frustules, about 6 weight % to about 10 weight % zinc salt (e.g., $Zn(NO_3)_2$), about 1 weight % to about 2 weight % of a base (e.g., ammonium hydroxide (NH_4OH)), about 1 weight % to about 5 weight % of an additive (e.g., hexamethylenetetramine (HMTA)), and about 78 weight % to about 91 weight % purified water. In some embodiments, forming the ZnO nanostructures comprises heating the mixture. The mixture may be heated using microwave. For example, the mixture may be heated in a microwave device to a temperature of about 100° C. to about 250° C. for about 30 minutes (min) to about 60 min (e.g., in a Monowave 300 for a smaller scale synthesis, such as for a mixture about 10 mL to about 30 mL, or a Masterwave BTR for a larger scale synthesis, such as for about a 1 liter (L) mixture, both commercially available from Anton Paar® GmbH). In some embodiments, the mixture may be stirred while being heated by the microwave. For example, the mixture may be stirred during heating by a magnetic stirrer at about 200 rotations per minute (RPM) to about 1000 RPM. Use of microwave heating may advantageously facilitate reduced duration of heating, providing a more efficient fabrication process.

In some embodiments, a frustule comprising ZnO nanostructures formed thereon comprises about 5 weight % to about 95 weight % of the ZnO, including about 10 weight % to about 95 weight %, about 20 weight % to about 95 weight %, about 30 weight % to about 95 weight %, about 40 weight % to about 95 weight %, or about 50 weight % to about 95 weight %, the remaining mass being the frustule. In some embodiments, a frustule comprising ZnO nanostructures formed thereon comprises about 5 weight % to about 95 weight % of the frustule, the remaining mass being the ZnO. In some embodiments, a frustule comprising ZnO nanostructures formed thereon comprises about 40 weight % to about 50 weight % of the frustule, the remaining mass being the ZnO. In some embodiments, a frustule comprising ZnO nanostructures formed thereon comprises about 50 weight % to about 60 weight % of the ZnO, the remaining mass being the ZnO. In some embodiments, a mass of the ZnO to a mass of the frustule can be about 1:20 to about 20:1, including about 1:15 to about 20:1, about 1:10 to about 20:1, about 1:1 to about 20:1, about 2:1 to about 10:1, or about 2:1 to about 9:1. The ZnO nanostructures preferably have a mass greater than a mass of the frustules prior to coating. In some embodiments, the mass of the ZnO nanostructures to the mass of the frustule can be greater than about 1:1, about 10:1, or about 20:1. In certain such embodiments, an upper limit may be based on, for example, openness of pores of the frustules (e.g., ZnO nanostructures not completely occluding the pores).

In some embodiments, a mass of the ZnO to a mass of the frustule can be about 1:20 to about 100:1, including about 1:1 to about 100:1, about 10:1 to about 100:1, about 20:1 to about 100:1, about 40:1 to about 100:1, about 60:1 to about 100:1, or about 80:1 to about 100:1. In some embodiments, the mass of the ZnO nanostructures to the mass of the frustule can be greater than about 30:1, about 40:1, about 50:1, about 60:1, about 70:1, about 80:1 or about 90:1. In some embodiments, a mass of the ZnO nanostructures to a mass of the frustule can be selected to provide desired device performance.

In some embodiments, pores of the frustules may be occluded by the nanostructures. For example, ZnO nanostructures may be formed on surfaces of the frustules, including surfaces within pores of the frustules, such that the ZnO nanostructures may occlude or substantially occlude some or all of the pores of the frustules.

The mass of the ZnO nanostructures may be determined by weighing the frustules before and after coating with the difference being the mass of the ZnO nanostructures. In some embodiments, the composition of the mixture for forming ZnO nanostructures can be selected such that ZnO covered frustules comprising a desired ZnO weight % can be formed. In some embodiments, the weight % of ZnO on frustule surfaces can be selected based on a desired mass of surface active material on an opposing energy storage device electrode. For example, the composition of the mixture for forming the ZnO nanostructures can be selected based on the mass of an oxide of manganese in an opposing energy storage electrode, such as the mass of one or more of MnO, Mn_2O_3, Mn_3O_4 and MnOOH. For example, based on stoichiometric calculations, a mass of Mn_{203} in an energy storage device electrode can be at least about 2.5 times that of ZnO in an opposing electrode.

Referring to FIG. **5**O, a SEM image at 500× magnification of a plurality of frustules **70** having ZnO nanostructures formed thereon is shown. The frustules **70** covered with ZnO nanostructures were first seeded with ZnO using a mixture consisting essentially of about 2 weight % to about 5 weight % frustules, about 0.1 weight % to about 0.5 weight % $Zn(CH_3COO)_2$, and about 94.5 weight % to about 97.9 weight % ethanol. The mixture for forming ZnO seeded frustules was heated to a temperature greater than about 80° C. for a duration to form the ZnO seeded frustules and achieve desired drying of the ZnO seeded frustules. Subsequently, ZnO nanostructures were formed on the ZnO seeded frustules using a mixture consisting essentially of about 1 weight % to about 5 weight % ZnO seeded frustules,

about 6 weight % to about 10 weight % $Zn(NO_3)_2$, about 1 weight % to about 2 weight % ammonium hydroxide (NH_4OH), about 1 weight % to about 5 weight % hexamethylenetetramine (HMTA), and about 78 weight % to about 91 weight % purified water. The mixture was heated using microwave to a temperature of about 100° C. to about 250° C. for about 30 minutes (min) to about 60 min to facilitate formation of the ZnO nanostructures and drying of the frustules. As shown in FIG. **5**O, unexpectedly, the plurality of frustules **70** having ZnO nanostructures formed thereon did not or substantially did not agglomerate. Each frustule **70** was individually covered or substantially covered by ZnO nanostructures. Each of the frustules **70** having ZnO nanostructures formed thereon shown in FIG. **5**O included about 50% to about 60% by weight of ZnO. FIG. **5**P shows a SEM image at 5 k× magnification of an individual frustule **70** having ZnO nanostructures formed thereon. The ZnO nanostructures on the frustule **70** of FIG. **5**P were formed using the process described with reference to FIG. **5**O. As shown in FIG. **5**P, the frustule **70** is covered by ZnO nanoflakes **78**. As shown in FIG. **5**P, the frustule **70** comprising ZnO nanoflakes **78** formed thereon is porous. For example, the ZnO nanoflakes **78** did not occlude pores of the frustules **70**, advantageously facilitating transport of electrolyte through an electrode comprising the frustules **70** having the ZnO nanoflakes **78** formed thereon.

Examples of suitable Zn salts which can be used for both ZnO seeding and nanostructures growth include: zinc acetate hydrate, zinc nitrate hexahydrate, zinc chloride, zinc sulfate, sodium zincate, combinations thereof, and/or the like.

Examples of suitable bases for ZnO nanostructures growth may include: sodium hydroxide, ammonium hydroxide, potassium hydroxide, tetramethylammonium hydroxide, lithium hydroxide, hexamethylenetetramine, ammonia solutions, sodium carbonate, ethylenediamine, combinations thereof, and/or the like.

Examples of suitable solvents for formation of ZnO nanostructures include one or more alcohols. Solvents described herein as being suitable for Ag nanostructures growth may also be suitable for ZnO nanostructure formation.

Examples of additives that may be used for nanostructures morphology control may include tributylamine, triethylamine, triethanolamine, diisopropylamine, ammonium phosphate, 1,6-hexadianol, triethyldiethylnol, isopropylamine, cyclohexylamine, n-butylamine, ammonium chloride, hexamethylenetetramine, ethylene glycol, ethanolamine, polyvinylalcohol, polyethylene glycol, sodium dodecyl sulphate, cetyltrimethyl ammonium bromide, carbamide, combinations thereof, and/or the like.

Example Process of Forming Carbon Nanotubes on a Surface of a Diatom Frustule

Carbon nanotubes (e.g., multiwall and/or single-wall) can be grown on a diatom surface (e.g., inside and/or outside) by chemical vapor deposition technique and its varieties. In this technique, the diatoms are firstly coated with catalyst seeds and then a mixture of gases is introduced. One of the gases may be a reducing gas and another gas may be a source of carbon. In some embodiments, a mixture of gases may be used. In some embodiments, a neutral gas can be included for the concentration control (e.g., argon). Argon may also be used to carry liquid carbonaceous material (e.g., ethanol). The seeds for forming a carbon nanotube can be deposited as metals by such techniques as spray coating and/or introduced from a liquid, a gas, and/or a solid and reduced later under elevated temperatures by pyrolysis. The reduction of carbonaceous gases may occur at higher temperatures, for example in a range of about 600° C. to about 1100° C.

Both the seed coating process and gas reactions can be realized on frustules surfaces due to nanoporosity. Techniques have been developed for carbon nanotubes "forest" growth on different substrates including silicon, alumina, magnesium oxide, quartz, graphite, silicon carbide, zeolite, metals, and silica.

Examples of suitable metal compounds for growth of catalyst seeds can include nickel, iron, cobalt, cobalt-molybdenum bimetallic particles, copper (Cu), gold (Au), Ag, platinum (Pt), palladium (Pd), manganese (Mn), aluminum (Al), magnesium (Mg), chromium (Cr), antimony(Sn), aluminum-iron-molybdenum (Al/Fe/Mo), Iron pentacarbonyl ($Fe(CO)_5$), iron (III) nitrate hexahydrate ($Fe(NO_3)_3.6H_2O$), iron (III) nitrate hexahydrate ($COCl_2.6H_2O$) ammonium molybdate tetrahydrate ($(NH_4)_6Mo_7O_{24}.4H_2O$), ammonium molybdate tetrahydrate ($(NH_4)_6Mo_7O_{24}.4H_2O$) (MoO_2Cl_2) alumina nanopowder, mixtures thereof, and/or the like.

Examples of suitable reducing gases may include ammonia, nitrogen, hydrogen, mixtures thereof, and/or the like.

Examples of suitable gases which may serve as a source of carbon (e.g., carbonaceous gases) may include acetylene, ethylene, ethanol, methane, carbon oxide, benzene, mixtures thereof, and/or the like.

Example Processes of Forming Manganese-Containing Nanostructures on Surfaces of Diatom Frustules

In some embodiments, manganese-containing nanostructures can be formed on one or more surfaces of a frustule. In some embodiments, an oxide of manganese can be formed on one or more surfaces of a frustule. In some embodiments, nanostructures comprising oxide of manganese having the formula Mn_xO_y where x is about 1 to about 3 and where y is about 1 to about 4, can be formed on one or more surfaces of a frustule. For example, nanostructures comprising manganese dioxide (MnO_2), manganese (II, III) oxide (Mn_3O_4), manganese (II) oxide (MnO), and/or manganese (III) oxide (Mn_2O_3) can be formed on one or more surfaces of a frustule. In some embodiments, nanostructures comprising manganese oxyhydroxide (MnOOH) can be formed on one or more surfaces of a frustule. In some embodiments, a membrane of an energy storage device can include frustules having manganese-containing nanostructures. In some embodiments, a printed energy storage device (e.g., a battery, a capacitor, a supercapacitor, and/or a fuel cell) can include one or more electrodes having a plurality of frustules which comprise manganese-containing nanostructures. In some embodiments, an ink used for printing a film can comprise a solution in which frustules comprising manganese-containing nanostructures are dispersed.

In some embodiments, one or more electrodes of a battery can include frustules comprising manganese-containing nanostructures on one or more surfaces (e.g., an electrode of a zinc-manganese battery). A charged battery can include a first electrode including frustules comprising nanostructures comprising manganese dioxide (MnO_2) and a second electrode comprising zinc (e.g., frustules comprising a zinc coating). In some embodiments, the second electrode can comprise other materials. A discharged battery can include a first electrode including frustules comprising nanostructures comprising manganese (II, III) oxide (Mn_3O_4), manganese (II) oxide (MnO), manganese (III) oxide (Mn_2O_3), and/or manganese oxyhydroxide (MnOOH) and a second electrode including zinc oxide (ZnO) (e.g., frustules comprising nanostructures comprising zinc oxide). In some embodiments, the second electrode of the discharged battery can comprise other materials. In some embodiments, a charged battery can

include a first electrode comprising frustules having manganese (II, III) oxide (Mn_3O_4), manganese (II) oxide (MnO), manganese (III) oxide (Mn_2O_3), and/or manganese oxyhydroxide (MnOOH) nanostructures formed thereon and a second opposing electrode comprising ZnO nanostructures formed thereon. In some embodiments, the battery can be a rechargeable battery.

A method of forming manganese-containing nanostructures on a diatom frustule portion can include adding the frustules to an oxygenated manganese acetate solution, and heating the frustules and the oxygenated manganese acetate solution. An example of a process for forming Mn_3O_4 on one or more surfaces of a frustule is provided. For example, pure water (e.g., pure water commercially available from EMD Millipore Corporation, of Billerica, Mass.) can be bubbled with oxygen gas (O_2) for a duration of about 10 minutes (min) to about 60 min (e.g., O_2 purging) to form oxygenated water. Manganese(II) acetate ($Mn(CH_3COO)_2$) can then be dissolved in the oxygenated water at a concentration of about 0.05 moles/liter (M) to about 1.2 M to form an oxygenated manganese acetate solution.

Frustules can be added to the oxygenated manganese acetate solution. Frustules added to the oxygenated manganese acetate solution may not have any previously formed nanostructures and/or coatings on frustule surfaces. In some embodiments, frustules added to the oxygenated manganese acetate solution can have one or more nanostructures and/or coatings on frustule surfaces. In some embodiments, frustules added to the oxygenated manganese acetate solution can have one or more nanostructures and/or coatings on at least some portions of the frustule surfaces. For example, frustules may have carbon-containing nanostructures on portions of frustule surfaces such that manganese-containing nanostructures formed according to one or more processes as described herein can be interspersed amongst the carbon-containing nanostructures. In some embodiments, carbon-containing nanostructures can include reduced graphene oxide, carbon nanotubes (e.g., single wall and/or multi-wall), and/or carbon nano-onions. Carbon-containing nanostructures can be formed on frustule surfaces according to one or more processes as described herein or other processes.

In some embodiments, frustules can be added to the oxygenated manganese acetate solution such that the solution comprises about 0.01 weight % to about 1 weight % of frustules. In some embodiments, other Mn^{2+} salts can be suitable. In some embodiments, other oxidizing agents (e.g., peroxides) can be suitable.

In some embodiments, growth of manganese-containing nanostructures can be conducted using a thermal technique and/or a microwave technique. In some embodiments, desired growth of nanostructures can involve a longer duration when using a thermal method. For example, a thermal technique may include using thermal heating in the nanostructure growth process. An example of a thermal method of growing nanostructures may include mixing (e.g., by stirring using any number of suitable techniques) frustules in the oxygenated manganese acetate solution for a duration of about 15 hours to about 40 hours (e.g., about 24 hours), while maintaining the mixture at a temperature of about 50 degrees C. (° C.) to about 90° C. (e.g., at about 60° C.). In some embodiments, the temperature of the mixture can be maintained by thermally heating the mixture.

In some embodiments, a microwave method of growing nanostructures can facilitate a shorter nanostructure growth process and/or facilitate a scalable nanostructure growth process. For example, a microwave method of nanostructure growth may include using microwave heating in the nanostructure growth process. An example of a nanostructure growth process using the microwave technique may include adding frustules to the oxygenated manganese acetate solution, and maintaining the mixture at a temperature of about 50° C. to about 150° C. for about 10 minutes (min) to about 120 min. The mixture may be stirred while it is being maintained at the temperature.

In some embodiments, manganese-containing structures having a reddish-brown color (e.g., after washing and drying) can form on one or more surfaces of frustules using one or more processes described herein. In some embodiments, the manganese oxide structures can have a tetrahedral shape. A reddish-brown color may indicate presence of manganese (II, III) oxide (Mn_3O_4). In some embodiments, formation of tetrahedral nanocrystals can indicate presence of manganese (II, III) oxide (Mn_3O_4).

FIG. **5**Q is a scanning electron microscope (SEM) image at 20 k× magnification of an example of a frustule **80** having nanostructures comprising manganese(II, III) oxide (Mn_3O_4) **82** on or more of its surfaces, where the nanostructures **82** are formed using a microwave method of nanostructure growth. FIG. **5**R is a SEM image at 50 k× magnification of the frustule **80** shown in FIG. **5**Q. The nanostructures **82** comprising manganese(II, III) oxide (Mn_3O_4) shown in FIGS. **5**Q and **5**R can be formed by using an oxygenated solution having a concentration of about 0.15 M manganese acetate prepared by bubbling oxygen gas (O_2) through pure water for a duration of about 30 min. For example, commercial grade oxygen gas (e.g., purity level of greater than 95%, such as at least about 97% pure, or at least about 99% pure) can be used. For example, oxygen gas having a purity of at least about 97% can be bubbled through a glass frit into a vial (e.g., a vial having a volume of about 20 milliliter (mL)) containing about 15 mL of pure water for a duration of about 30 minutes at room temperature (e.g., at about 25° C.). A weight of 0.55 grams (g) of manganese acetate tetrahydrate (e.g., commercially available from Sigma-Aldrich Corp.) can be dissolved in the oxygenated pure water. A weight of 0.005 grams (g) of diatoms can be added to the oxygenated manganese-containing solution. Then the vial containing the mixture comprising the added frustules can be placed in a microwave (e.g., Monowave 300 microwave, commercially available from Anton Paar® GmbH), and the synthesis can be conducted at a desired temperature for a desired period of time. The mixture comprising the solution and frustules can be maintained for about 30 minutes at a temperature of about 60° C., for example under continues stirring (e.g., with a magnetic stir bar, such as at a rotation speed of about 600 rpm). In some embodiments, the mixture can be subsequently diluted with water, and centrifuged (e.g., at about 5000 rpm for about 5 min) such that the supernatant can be discarded. In some embodiments, the precipitate can be diluted with water again, then dispersed (e.g., shaking, and/or vortexing) and again centrifuged such that the supernatant can be discarded. The precipitate can then be dried at about 70° C. to about 80° C. in a vacuum oven.

Referring to FIG. **5**R, the nanostructures **82** can have a tetrahedral shape. It was observed that the manganese(II, III) oxide (Mn_3O_4) structures surprisingly grow on the surface of the frustules rather than forming in the solution separate from frustules.

FIG. **5**S is a transmission electron microscope (TEM) image of nanostructures **82** formed on surfaces of the frustule shown in FIGS. **5**Q and **512**. One or more individual atoms of the nanostructures **82** can be seen, and a scale is

provided for size comparison. FIG. **5**T shows an electron diffraction image of a manganese(II, III) oxide (Mn_3O_4) particle.

In some embodiments, a shape and/or dimension of nanostructures formed on a frustule surface can depend on a parameter of the nanostructure formation process. For example, morphology of nanostructures can depend on a solution concentration and/or a level of oxygenation of the solution. FIG. **5**U is a SEM image at 10 k× magnification of a frustule **90** comprising manganese-containing nanostructures **92** formed on its surfaces, where the manganese-containing nanostructures **92** were formed using a solution having a higher oxygen concentration (e.g., oxygen purging of water for a duration of about 40 minutes) and higher manganese concentration (e.g., a manganese acetate concentration of about 1 M), as compared to the process used in the formation of nanostructures **82** shown in FIGS. **5**Q and **5**R. For example, the nanostructures **92** can be formed on frustules **90** according to the process as described with reference to formation of nanostructures **82** (e.g., of FIGS. **5**Q and **5**R), except with the following differences: oxygen gas bubbling of the pure water can be performed for a duration of about 40 minutes, with the addition of about 0.9 grams (g) of manganese acetate to the oxygenated pure water, and about 0.01 grams (g) of diatoms can be added to the manganese-containing solution, and the mixture comprising the diatoms and manganese-containing solution can be microwaved at a temperature of about 150° C.

As shown in FIG. **5**U, the nanostructures **92** can have an elongate fiber-like shape. In some embodiments, the nanostructures **92** can have a thin elongate shape (e.g., thin whisker-like structure). In some embodiments, formation of fiber-like structures can indicate presence of manganese oxyhydroxide (MnOOH).

In some embodiments, forming nanostructures comprising one or more oxides of manganese having the formula Mn_xO_y where x is about 1 to about 3 and where y is about 1 to about 4, on one or more surfaces of a frustule can include combining frustules with a manganese source, such as a manganese salt (e.g., manganese acetate ($Mn(CH_3COO)_2$)) and a base (e.g., ammonium hydroxide (NH_4OH)) in oxygenated water. In some embodiments, forming the Mn_xO_y nanostructures on one or more surfaces of frustules can include forming a mixture comprising the following composition: about 0.5 weight % to about 2 weight % of frustules, about 7 weight % to about 10 weight % of $Mn(CH_3COO)_2$, about 5 weight % to about 10 weight % of NH_4OH and about 78 weight % to about 87.5 weight % of oxygenated purified water. In some embodiments, oxygenated purified water for the mixture can be prepared by bubbling oxygen through the purified water for about 10 minutes to about 30 minutes. The mixture may be heated using microwave to facilitate formation of the Mn_xO_y nanostructures (e.g., in a Monowave 300 for a smaller scale synthesis, such as for a mixture about 10 mL to about 30 mL, or a Masterwave BTR for a larger scale synthesis, such as for about a 1 liter (L) mixture, both commercially available from Anton Paar® GmbH). For example, the mixture may be heated using a microwave to a temperature of about 100° C. to about 250° C. for about 30 minutes to about 60 minutes. In some embodiments, the mixture can be stirred while being heated, for example by a magnetic stirrer at about 200 rotations per minute (RPM) to about 1000 RPM.

In some embodiments, a frustule comprising an oxide of manganese (e.g., an oxide having the formula Mn_xO_y where x is about 1 to about 3 and y is about 1 to about 4) nanostructures formed thereon comprises about 5 weight % to about 95 weight % of the oxide of manganese, including about 30 weight % to about 95 weight %, about 40 weight % to about 95 weight %, about 40 weight % to about 85 weight %, about 50 weight % to about 85 weight %, about 55 weight % to about 95 weight %, or about 75 weight % to about 95 weight %, the remaining mass being the frustule. In some embodiments, a frustule comprising an oxide of manganese (e.g., an oxide having the formula Mn_xO_y where x is about 1 to about 3 and y is about 1 to about 4) nanostructures formed thereon comprises about 5 weight % to about 50 weight % of the frustule, the remaining mass being the oxide of manganese nanostructures. In some embodiments, a mass of the oxide of manganese nanostructures to a mass of the frustule can be about 1:20 to about 20:1, including about 1:15 to about 20:1, about 1:10 to about 20:1, about 1:1 to about 20:1, about 5:1 to about 20:1, about 1:1 to about 10:1, or about 2:1 to about 9:1. The oxide of manganese nanostructures preferably have a mass greater than a mass of the frustules prior to coating. In some embodiments, a ratio of the mass of the oxide of manganese nanostructures to the mass of the frustule can be greater than about 1:1, about 10:1, or about 20:1. In certain such embodiments, an upper limit may be based on, for example, openness of pores of the frustules (e.g., the oxide of manganese nanostructures not completely occluding the pores).

In some embodiments, pores of the frustules may be occluded by the nanostructures. For example, oxide of manganese nanostructures may be formed on surfaces of the frustules, including surfaces within pores of the frustules, such that the oxide of manganese nanostructures may occlude or substantially occlude some or all of the pores of the frustules.

In some embodiments, a mass of the oxide of manganese nanostructures to a mass of the frustule can be about 1:20 to about 100:1, including about 1:1 to about 100:1, about 10:1 to about 100:1, about 20:1 to about 100:1, about 40:1 to about 100:1, about 60:1 to about 100:1, or about 80:1 to about 100:1. In some embodiments, the mass of the manganese nanostructures to the mass of the frustule can be greater than about 30:1, about 40:1, about 50:1, about 60:1, about 70:1, about 80:1 or about 90:1. In some embodiments, a mass of the manganese nanostructures to a mass of the frustule can be selected to provide desired device performance.

The mass of the oxide of manganese nanostructures may be determined by weighing the frustules before and after coating with the difference being the mass of the oxide of manganese nanostructures. In some embodiments, the composition of the mixture for forming oxide of manganese nanostructures can be selected such that a desired oxide of manganese weight % can be formed. In some embodiments, the weight % of the oxide of manganese on frustule surfaces can be selected based on a desired mass of surface active material on an opposing energy storage device electrode. For example, the composition of the mixture for forming the oxide of manganese nanostructures can be selected based on the mass of ZnO in an opposing energy storage device electrode. In some embodiment, based on stoichiometric calculations, a mass of Mn_2O_3 in an energy storage device electrode can be at least about 2.5 times that of ZnO in an opposing electrode.

FIG. **5**V is a SEM image at 20 k× magnification of a frustule **94** comprising oxides of manganese nanostructures **96** formed thereon. The nanostructures **96** included a mixture of different oxides of manganese, the oxides having the formula Mn_xO_y where x is about 1 to about 3 and y is about 1 to about 4. As shown in FIG. **5**V, the frustule **94** is thickly

covered by the oxide of manganese nanostructures **96**. FIG. **5**W is a SEM image at 50 k× magnification of a cross-sectional view of a frustule **94** comprising oxides of manganese nanostructures **96** (e.g., oxides having the formula Mn_xO_y where x is about 1 to about 3 and y is about 1 to about 4) formed thereon. The frustule **94** was cut using focused ion beam (FIB) technique and a cross-section view of the cut frustule **94** is shown in FIG. **5**W. As shown in FIG. **5**W, the oxides of manganese nanostructures **96** can be formed on interior and exterior surfaces of the frustule **94**, and a volume of the nanostructures **96** can be greater than a volume of the frustule **94**. FIG. **5**X is a SEM image at 100 k× magnification of a sidewall of a frustule **94** comprising oxides of manganese nanostructures **96** (e.g., oxides having the formula Mn_xO_y where x is about 1 to about 3 and y is about 1 to about 4) formed thereon. As shown in FIG. **5**X, a sidewall of the frustule **94** can be covered by the oxides of manganese nanostructures **96** while pores on the sidewall are not occluded. A frustule having oxide of manganese nanostructures formed thereon without or substantially without occluding pores of the frustule can advantageously facilitate transport of electrolyte through an electrode comprising the frustule covered by the oxide of manganese nanostructures.

The frustules **94** comprising the oxides of manganese nanostructures **96** formed thereon shown in FIGS. **5**V through **5**X were formed using a mixture consisting essentially of about 0.5 weight % to about 2 weight % of frustules, about 7 weight % to about 10 weight % of $Mn(CH_3COO)_2$, about 5 weight % to about 10 weight % of NH_4OH and about 78 weight % to about 87.5 weight % of oxygenated purified water. The mixture was heated using microwave to a temperature of about 100° C. to about 250° C. for about 30 minutes to about 60 minutes. As shown in FIGS. **5**V through **5**X, the frustules **94** were thickly covered by the oxides of manganese nanostructures **96**. For example, about 75 weight % to about 95% of oxides of manganese nanostructure covered frustule was the nanostructures and the remaining mass was the mass of the frustule.

Combination of Coatings

In some embodiments, a combination of coating can also be possible. For example, a surface of a frustule may include both a nickel coating and a coating of carbon nanotubes (e.g., such a frustule can be used for energy storage devices, including supercapacitors).

FIG. **6** schematically illustrates an example embodiment of an energy storage device **100**. FIG. **6** may be a cross-section or elevational view of the energy storage device **100**. The energy storage device **100** includes a first electrode **140** and a second electrode **150**, for example a cathode and an anode, respectively or irrespectively. The first and second electrodes **140**, **150** are separated by a separator **130**. The energy storage device **100** may optionally include one or more current collectors **110**, **120** electrically coupled to one or both of the electrodes **140**, **150**.

In some embodiments, the energy storage device **100** comprises a first electrode **140**, a second electrode **150**, and/or a separator **130**, any of which may be a membrane or layer, including a deposited membrane or layer.

A current collector **110**, **120** may include any component that provides a path for electrons to external wiring. For example, a current collector **110**, **120** may be positioned adjacent to the surface of the first and second electrodes **140**, **150** to allow energy flow between the electrodes **140**, **150** to be transferred to an electrical device. In the embodiment shown in FIG. **6**, a first current collector layer **110** and a second collector layer **120** are adjacent to the surface of the first electrode **140** and to the surface of the second electrode **150**, respectively. The current collectors **110**, **120** are adjacent to surfaces opposite to surfaces of the electrode **140**, **150**, respectively, that are adjacent to the separator layer **130**.

In some embodiments, the current collector **110**, **120** comprises an electrically conductive foil (e.g., graphite, such as graphite paper, graphene, such as graphene paper, aluminum (Al), copper (Cu), stainless steel (SS), carbon foam). In some embodiments, the current collector **110**, **120** comprises an electrically conductive material deposited on a substrate. For example, the current collector **110**, **120** can comprise an electrically conductive material printed on a substrate. In some embodiments, a suitable substrate can include polyester, polyimide, polycarbonate, cellulose (e.g., cardboard, paper, including coated paper, such as plastic coated paper, and/or fiber paper). In some embodiments, the conductive material can comprise silver (Ag), copper (Cu), carbon (C) (e.g., carbon nanotubes, graphene, and/or graphite), aluminum (Al), nickel (Ni), combinations thereof, and/or the like. Examples of a conductive material comprising nickel suitable for current collectors are provided in PCT Patent Application No. PCT/US2013/078059, entitled "NICKEL INKS AND OXIDATION RESISTANT AND CONDUCTIVE COATINGS," filed Dec. 27, 2013, which is incorporated herein by reference in its entirety.

In some embodiments, an energy storage device **100** includes at least one layer or membrane comprising frustules. For example, an energy storage device **100** may include a layer or membrane comprising a dispersion including frustules. The layer or membrane comprising frustules may include, for example, the first electrode **140**, the second electrode **150**, the separator **130**, the first collector layer **110**, the second collector layer **120**, combinations thereof, and/or the like. In some embodiments, the energy storage device **100** includes frustules having a uniform or substantially uniform shape, dimension (e.g., diameter, length), material, porosity, a surface modifying material and/or structure, any other suitable feature or attribute, combinations thereof, and/or the like. In embodiments in which a plurality of layers of the energy storage **100** device comprise frustules, the frustules may be the same or substantially the same (e.g., having similar dimensions) or may be different (e.g., insulating in the separator **130** and conductively coated in an electrode **140**, **150**).

The energy storage device **100** may include one or more layers or membranes comprising frustules having a length in a range from about 0.5 μm to about 50 μm, from about 1 μm to about 50 μm, from about 1 μm to about 40 μm, from about 1 μm to about 30 μm, from about 1 μm to about 20 μm, from about 1 μm to about 10 μm, from about 5 μm to about 50 μm, from about 5 μm to about 40 μm, from about 5 μm to about 30 μm, from about 5 μm to about 20 μm, and from about 5 μm to about 10 μm. In some embodiments, the cylindrically shaped frustules have a length of no more than about 50 μm, no more than about 40 μm, no more than about 30 μm, no more than about 20 μm, no more than about 15 μm, no more than about 10 μm, or no more than about 5 μm. Other frustule lengths are also possible.

The energy storage device **100** may comprise one or more layers or membranes comprising frustules having diameters within a range of from about 0.5 μm to about 50 μm, from about 1 μm to about 50 μm, from about 1 μm to about 40 μm, from about 1 μm to about 30 μm, from about 1 μm to about 20 μm, from about 1 μm to about 10 μm, from about 5 μm to about 50 μm, from about 5 μm to about 40 μm, from about 5 μm to about 30 μm, from about 5 μm to about 20 μm, and

from about 5 μm to about 10 μm. In some embodiments, the cylindrically shaped frustules have a diameter of no more than about 50 μm, no more than about 40 μm, no more than about 30 μm, no more than about 20 μm, no more than about 15 μm, no more than about 10 μm, no more than about 5 μm, no more than about 2 μm, or no more than about 1 μm. Other frustule diameters are also possible.

The energy storage device **100** may comprise frustules having a uniform or substantially uniform within-frustule porosity and/or frustule-to-frustule porosity and/or frustules having porosity within a particular range. In some embodiments, the energy storage device **100** comprises one or more layers or membranes including frustules having porosities in a range of from about 10% to about 50%, from about 15% to about 45%, and from about 20% to about 40%. In some embodiments, pores on frustule surfaces can have a size (e.g., a length, width, diameter, and/or longest dimension) of about 1 nanometer (nm) to about 500 nm. For example, pores on a frustule surface can have a size that can facilitate desired energy storage device performance (e.g., diffusion of electrolytic ions of the energy storage device to facilitate a desired electrical performance of the device). Other frustule porosities are also possible.

As described herein, an energy storage device **100** may include one or more layers or membranes including frustules **50** comprising no or substantially no surface modifying material and/or surface modifying structures **52** applied or formed on a surface of the frustules **50** and/or frustules **50** comprising a material and/or structures **52** applied or formed on a surface of the frustules **50** to modify a characteristic or attribute of the frustules **50**. For example, the separator **130** may comprise frustules **50** comprising no or substantially no surface modifying material and/or surface modifying structures **52** applied or formed on a surface of the frustules **50**, and at least one of the electrodes **140**, **150** may comprise frustules **50** comprising a material and/or structures **52** applied or formed on a surface of the frustules **50** to modify a characteristic or attribute of the frustules **50**. For another example, the separator **130** may comprise some frustules **50** comprising no or substantially no surface modifying material and/or surface modifying structures **52** applied or formed on a surface of the frustules **50** and some frustules **50** comprising a material and/or structures **52** applied or formed on a surface of the frustules **50** to modify a characteristic or attribute of the frustules **50**.

In some embodiments, the energy storage device **100** comprises frustules having a non-uniform or substantially non-uniform shape, dimension, porosity, surface modifying material and/or structure, another suitable attribute, and/or combinations thereof.

In some embodiments, one or more layers or membranes of the energy storage device **100** may be printed. In some embodiments, one or more layers or membranes of the energy storage device **100** can be printed from an ink. In some embodiments, the ink can be printed using various techniques described herein, including stenciling, screen printing, rotary printing, die coating, rotogravure printing, flexo and pad printing, combinations thereof, and/or the like. In some embodiments, a viscosity of the ink can be adjusted based on the printing technique applied (e.g., a desired viscosity may be achieved by adjusting, for example, a quantity of the solvent used for the ink).

In some embodiments, current collectors may be printed using a conductive ink. For example, the current collector can comprise an electrically conductive material printed on a substrate. In some embodiments, a suitable substrate can include polyester, polyimide, polycarbonate, cellulose (e.g., cardboard, paper, including coated paper, such as plastic coated paper, and/or fiber paper). In some embodiments, the conductive ink may comprise aluminum, silver, copper, nickel, bismuth, conductive carbon, carbon nanotubes, graphene, graphite, combinations thereof, and/or the like. In some embodiments, the conductive material can comprise silver (Ag), copper (Cu), carbon (C) (e.g., carbon nanotubes, graphene, and/or graphite), aluminum (Al), nickel (Ni), combinations thereof, and/or the like. Examples of a conductive material comprising nickel suitable for current collectors are provided in PCT Patent Application No. PCT/US2013/078059, entitled "NICKEL INKS AND OXIDATION RESISTANT AND CONDUCTIVE COATINGS," filed Dec. 27, 2013, which is incorporated herein by reference in its entirety.

In some embodiments, an ink can be prepared using a plurality of frustules. The ink comprising the frustules may be printed to form a component of an energy storage device, such as an electrode or a separator of an energy storage device. In some embodiments, the ink may comprise frustules comprising nanostructures formed thereon, including one or more nanostructures described herein. For example, an ink comprising nanostructure covered frustules may be printed to form an electrode of the energy storage device **100**. In some embodiments, the ink may comprise frustules having no or substantially no nanostructures formed thereon. For example, an ink comprising frustules having no or substantially no surface modifications may be printed to form the separator **130** of the energy storage device **100**.

FIGS. **7**A through **7**E are schematic diagrams showing cross-sectional views of examples of energy storage devices. In some embodiments, the energy storage devices of FIGS. **7**A through **7**E are printed energy storage devices. For example, the energy storage devices of FIGS. **7**A through **7**E may include a first current collector **110**, a second current collector **120**, a first electrode **140**, a second electrode **150** and a separator **130**, which are all printed. For example, one or more layers of the printed energy storage devices of FIGS. **7**A through **7**C can be printed on separate substrates and the separate substrates can be subsequently assembled together to form the energy storage device, while layers of the energy storage devices of FIGS. **7**D and **7**E can be printed on one substrate.

In some embodiments, FIGS. **7**A through **7**C are schematic diagrams showing cross-sectional views of examples of partially printed energy storage devices, while FIGS. **7**D and **7**E are schematic diagrams showing cross-sectional views of fully printed energy storage devices, during various stages of the respective manufacturing processes. The energy storage devices shown in FIGS. **7**A through **7**C may include current collectors **110**, **120**, which may be printed (e.g., over separate substrates) and/or not printed (e.g., acting as a substrate on which other layers are printed). FIGS. **7**D and **7**E show cross-sectional views of energy storage devices which include current collectors **110**, **120**, which may be printed (e.g., each over a substrate) or not printed (e.g., the first current collector **110** in FIG. **7**D acting as a substrate on which other layers are printed, the first and second current collectors **110**, **120** acting together as a substrate on which other layers are printed in FIG. **7**E).

In some embodiments, the first current collector **110**, second current collector **120**, first electrode **140**, second electrode **150**, and/or separator **130** of FIGS. **7**A through **7**E can have one or more properties and/or be fabricated as described herein. For example, the first current collector **110**, second current collector **120**, first electrode **140**, second electrode **150**, and/or separator **130** can be printed using one

or more techniques and/or ink compositions as described herein. For example, one of the electrodes **140**, **150** may comprise frustules including nanostructures comprising an oxide of manganese (e.g., oxide having the formula Mn_xO_y, where x is about 1 to about 3 and y is about 1 to about 4) and the other of the electrodes **140**, **150** may comprise frustules including nanostructures comprising zinc (e.g., ZnO), one or both of which may be printed from an ink. For another example, the separator **130** may comprise frustules comprising no or substantially no surface modification, which may be printed from an ink. As described herein, non-printed current collectors may comprise an electrically conductive foil, such as a foil comprising aluminum, copper, nickel, stainless steel, graphite (e.g., graphite paper), graphene (e.g., graphene paper), carbon nanotubes, carbon foam, combinations thereof, and the like. In some embodiments, the conductive foil can be laminated and have a polymer layer on one of its two opposing surfaces.

In FIG. **7**A, an energy storage device **200** includes a first structure **202** and a second structure **204**. The first structure **202** comprises a first electrode **140** over a first current collector **110** and a separator **130** over the first electrode **140**. The second structure **204** comprises a second electrode **150** over a second current collector **120**. In some embodiments, the first electrode **140** can be printed over the first current collector **110**. For example, the first electrode **140** can be printed directly on and in contact with the first current collector **110**. In some embodiments, the separator **130** can be printed over the first electrode **140**. For example, the separator **130** may be printed directly on and in contact with the first electrode **140**. In some embodiments, the separator **130** can be printed over the first electrode **140** such that the separator **130** and the first current collector **110** encapsulate or substantially encapsulate the first electrode **140**. In some embodiments, the second electrode **150** can be printed over the second current collector **120**, for example directly on and in contact with the second current collector **120**. In some embodiments, a process for fabricating the energy storage device **200** can include assembling together the first structure **202** and the second structure **204**. For example, fabricating the energy storage device **200** shown in FIG. **7**A can include bringing the second electrode **150** of the second structure **204** into contact with the separator **130** of the first structure **202** such that the separator **130** is between the first electrode **140** and the second electrode **150**.

FIG. **7**B shows an energy storage device **210** comprising a first structure **212** comprising a first electrode **140** over a first current collector **110** and a first portion of a separator **130** over the first electrode **140**. The energy storage device **210** may comprise a second structure **214** comprising a second electrode **150** over a second current collector **120**, and a second portion of the separator **130** over the second electrode **150**. In some embodiments, the second electrode **150** can be printed over the second current collector **120**. For example, the second electrode **150** can be printed on and in direct contact with the second current collector **120**. In some embodiments, the second portion of the separator **130** can be printed on and in direct contact with the second electrode **150**. For example, the second portion of the separator **130** can be printed on and in direct contact with the second electrode **150**. In some embodiments, the first electrode **140** can be printed over the first current collector **110**. For example, the first electrode **140** can be printed on and in direct contact with the first current collector **110**. In some embodiments, the first portion of the separator **130** can be printed over the first electrode **140**. For example, the first portion of the separator **130** can be printed on and in direct contact with the first electrode **140**. In some embodiments, the first and second portions of the separator **130** can be printed such that the first portion of the separator **130** and the first current collector **110** encapsulate or substantially encapsulate the first electrode **140**, and/or the second portion of the separator **130** and the second current collector **120** encapsulate or substantially encapsulate the second electrode **150**. In some embodiments, a process for fabricating the energy storage device **210** can include assembling together (e.g., coupling) the first structure **212** and the second structure **214** to form the energy storage device **210**. Assembling the first structure **212** and the second structure **214** may comprise providing the first and second portions of the separator **130** between the first electrode **140** and the second electrode **150**. For example, fabricating the energy storage device **210** shown in FIG. **7**B can include bringing the second portion of the separator **130** of the second structure **214** into contact with the first portion of the separator **130** of the first structure **212** such that the two portions of the separator **130** are between the first electrode **140** and the second electrode **150**.

As shown in FIG. **7**C, in some embodiments, an energy storage device **220** may comprise a first structure **222** comprising a first electrode **140** over a first current collector **110**, a separator **130** over the first electrode **140**, and a second electrode **150** over the separator **130**. The energy storage device **220** may comprise a second structure **224** comprising a second current collector **120**. In some embodiments, the first electrode **140** can be printed over the first current collector **110**. For example, the first electrode **140** can be printed on and in direct contact with the first current collector **110**. In some embodiments, the separator **130** can be printed over the first electrode **140**. For example, the separator **130** can be printed on and in direct contact with the first electrode **140**. In some embodiments, the separator **130** can be printed over the first electrode **140** such that the separator **130** and the first current collector **110** encapsulate or substantially encapsulate the first electrode **140**. In some embodiments, the second electrode **150** can be printed over the separator **130**. For example, the second electrode **150** can be printed on and in direct contact with the separator **130**. In some embodiments, assembling the energy storage device **220** includes coupling the first structure **222** and the second structure **224** to form the energy storage device **220**. In some embodiments, coupling the first structure **222** and the second structure **224** can include bringing the second current collector **120** into contact with the second electrode **150** such that the second electrode **150** is between the second current collector **120** and the separator **130**.

As described herein, FIGS. **7**D and **7**E are schematic diagrams of fully printed energy storage devices. FIG. **7**D shows an example of a vertically stacked energy storage device **230** comprising printed current collectors **110**, **120**, electrodes **140**, **150** and a separator **130**. Referring to FIG. **7**D, in some embodiments, a first current collector **110** of the energy storage device **230** can be printed on a substrate. In some embodiments, a first electrode **140** can be printed over the first current collector **110**. For example, the first electrode **140** can be printed on and in direct contact with the first current collector **110**. In some embodiments, a separator **130** can be printed over the first electrode **140**. For example, the separator **130** can be printed on and in direct contact with the first electrode **140**. In some embodiments, a second electrode **150** can be printed over the separator **130**. For example, the second electrode **150** can be printed on and in direct contact with the separator **130**. In some embodiments, a second current collector **120** can be subsequently printed

over the second electrode **150**. For example, the second current collector **120** can be printed on and in direct contact with the second electrode **150**. In some embodiments, the second current collector **120** can be printed over the second electrode **150** such that the second current collector **120** and the separator **130** encapsulate or substantially encapsulate the second electrode **150**. In some embodiments, the separator **130** can be printed over the first electrode **140** such that the separator **130** and the first current collector **110** encapsulate or substantially encapsulate the first electrode **140**.

Referring to FIG. **7**E, an energy storage device **240** having laterally spaced electrodes **140**, **150** is shown. The energy storage device **240** can include a first current collector **110** laterally spaced from a second current collector **120**, and a first electrode **140** and a second electrode **150** over the first current collector **110** and the second current collector **120**, respectively. A separator **130** can be over the first electrode **140** and the second electrode **150**. For example, the separator **130** can be formed between the first electrode **140** and the second electrode **150** such that electrodes **140**, **150** are electrically insulated from one another. In some embodiments, the separator **130** facilitates electrical insulation between the first current collector **110** and the second current collector **120**. In some embodiments, each of the first current collector **110**, the second current collector **120**, the first electrode **140**, the second electrode **150**, and the separator **130** can be printed. For example, the first current collector **110** and the second current collector **120** may be printed on a substrate. In some embodiments, the first electrode **140** can be printed on and in direct contact with the first current collector **110**. For example, the first electrode **140** can be printed on and in direct contact with the first current collector **110**. In some embodiments, the second electrode **150** can be printed over the second current collector **120**. For example, the second electrode **150** can be printed on and in direct contact with the second current collector **120**. In some embodiments, the separator **130** can be printed over the first electrode **140** and the second electrode **150**, such as on and in direct contact with both the first electrode **140** and the second electrode **150**. In some embodiments, the separator **130** can be printed over the first electrode **140** and the second electrode **150** such that the separator **130** and the first current collector **110** and the second current collector **120** can encapsulate or substantially encapsulate the first electrode **140** and the second electrode **150**, respectively. In some embodiments, first and second structures each similar to the first structure **202** and the second structure **204** of FIG. **7**A (e.g., comprising a current collector and an electrode, and optionally a separator) may be formed with different surface active materials (e.g., one or more oxides of manganese and ZnO) and then laterally coupled.

FIG. **8** shows an example embodiment of a separator layer or membrane **300** that may form part of an energy storage device (e.g., the separator **130** in any of the energy storage devices described with reference to FIGS. **6** and **7**A through **7**E). The separator **300** includes frustules **320**. In some embodiments, an energy storage device includes a separator layer or membrane **300** comprising frustules **320**. For example, an energy storage device may include a separator **300** comprising a dispersion including frustules **320**. As described herein, the frustules **320** may be sorted according to a shape, dimensions, material, porosity, combinations thereof, and/or the like, such that the separator **300** comprises frustules **320** having a uniform or substantially uniform shape, dimension (e.g., length, diameter), porosity, material, combinations thereof, and/or the like. For example, the separator **300** may include frustules **320** having a cylindrical or substantially cylindrical shape (e.g., as shown in FIG. **8**), a spherical or substantially spherical shape, another shape, and/or combinations thereof. In some embodiments, the separator **300** includes frustules **320** having a material and/or structures applied or formed on a surface of the frustules **320**. The separator **300** may comprise frustules **320** comprising no or substantially no surface modifying material and/or surface modifying structures applied or formed on a surface of the frustules **320** (e.g., as illustrated in FIG. **8**). The separator **300** may comprise frustules **320** comprising a material and/or structures applied or formed on a surface of the frustules **320** to modify a characteristic or attribute of the frustules **320**. The separator **300** may comprise some frustules **320** comprising no or substantially no surface modifying material and/or surface modifying structures applied or formed on a surface of the frustules **320** and some frustules **320** comprising a material and/or structures applied or formed on a surface of the frustules **320** to modify a characteristic or attribute of the frustules **320**.

The separator **300** may comprise frustules **320** having a mechanical strength sufficient to enable a stable or substantially stable separation between a first electrode **140** and a second electrode **150** of an energy storage device (e.g., any of the first electrode **140** and second electrode **150** of FIGS. **6** and **7**A through **7**E). In some embodiments, the separator **300** comprises frustules **320** configured to increase efficiency of an energy storage device, for example by enabling a reduced separation distance between a first electrode **140** and a second electrode **150** and/or by facilitating flow of ionic species between a first electrode **140** and a second electrode **150**. For example, frustules **320** may have a uniform or substantially uniform shape, dimension, porosity, surface modifying material and/or structures, combinations thereof, and/or the like, for improved energy storage device efficiency and/or mechanical strength. The separator **300** of an energy storage device may comprise cylindrical or substantially cylindrical frustules **320** including walls having a desired porosity, dimensions, and/or surface modifying material and/or structures.

The separator **300** may comprise one or more layers of frustules **320**. The separator **300** comprising frustules **320** may have a uniform or substantially uniform thickness. In some embodiments, thickness of a separator **300** comprising frustules **320** is as thin as possible. In some embodiments, thickness of a separator **300** comprising frustules **320** is from about 1 μm to about 100 μm, including from about 1 μm to about 80 μm, from about 1 μm to about 60 μm, from about 1 μm to about 40 μm, from about 1 μm to about 20 μm, from about 1 μm to about 10 μm, from about 5 μm to about 60 μm, from about 5 μm to about 40 μm, from about 5 μm to about 20 μm, from about 5 μm to about 15 μm, from about 5 μm to about 10 μm, from about 10 μm to about 60 μm, from about 10 μm to about 40 μm, from about 10 μm to about 20 μm, from about 10 μm to about 15 μm, and from about 15 μm to about 30 μm. In some embodiments, a separator comprises a thickness of less than about 100 μm, less than about 90 μm, less than about 80 μm, less than about 70 μm, less than about 60 μm, less than about 50 μm, less than about 40 μm, less than about 30 μm, less than about 20 μm, less than about 15 μm, less than about 10 μm, less than about 5 μm, less than about or 2 μm, less than about or 1 μm, and including ranges bordering and including the foregoing values. Other thicknesses of the separator **300** are also possible. For example, the separator **300** may comprise a single layer of frustules **320** such that the thickness of the

separator **300** may depend at least in part on a dimension of the frustules **320** (e.g., a longest axis, a length, or a diameter).

The separator **300** may comprise frustules **320** having a non-uniform or substantially non-uniform shape, dimension, porosity, surface modifying material and/or structure, combinations thereof, and/or the like.

In some embodiments, the separator **300** can include hollow and/or solid microspheres made from non-electrically conducting materials. For example, the separator **300** can include hollow and/or solid microspheres made of glass, alumina, silica, polystyrene, melamine, combinations thereof, and/or the like. In some embodiments, the microspheres can have size to facilitate printing of the separator **300**. For example, the separator **300** can include microspheres having a diameter of about 0.1 microns (μm) to about 50 μm. Examples of separators comprising hollow and/or solid microspheres are provided in U.S. patent application Ser. No. 13/223,279, entitled, "PRINTABLE IONIC GEL SEPARATION LAYER FOR ENERGY STORAGE DEVICES," filed Aug. 9, 2012, which is incorporated herein by reference in its entirety.

In some embodiments, the separator **300** comprises a material configured to reduce electrical resistance between a first electrode **140** and a second electrode **150** of an energy storage device. For example, referring again to FIG. **8**, in some embodiments, the separator **300** comprises an electrolyte **340**. The electrolyte **340** may include any material that facilitates the conductivity of ionic species, including, for example, a material comprising mobile ionic species that can travel between a first electrode **140** and a second electrode **150** of an energy storage device. The electrolyte **340** may comprise any compound that may form ionic species, including but not limited to sodium sulfate (Na_2SO_4), lithium chloride (LiCl), and/or potassium sulfate (K_2SO_4). In some embodiments, the electrolyte **340** comprises an acid, a base, or a salt. In some embodiments, the electrolyte **340** comprises a strong acid, including but not limited to sulfuric acid (H_2SO_4) and/or phosphoric acid (H_3PO_4), or a strong base, including but not limited to sodium hydroxide (NaOH) and/or potassium hydroxide (KOH). In some embodiments, the electrolyte **340** comprises a solvent having one or more dissolved ionic species. For example, the electrolyte **340** may comprise an organic solvent. In some embodiments, the electrolyte **340** includes an ionic liquid or an organic liquid salt. The electrolyte **340** may comprise an aqueous solution having an ionic liquid. The electrolyte **340** may comprise a salt solution having an ionic liquid. In some embodiments, the electrolyte **340** comprising an ionic liquid includes propylene glycol and/or acetonitrile. In some embodiments, the electrolyte **340** comprising an ionic liquid includes an acid or base. For example, the electrolyte **340** may comprise an ionic liquid combined with potassium hydroxide (e.g., addition of a 0.1 M solution of KOH).

In some embodiments, the electrolyte **340** can include one or more ionic liquids and/or one or more salts described in U.S. patent application Ser. No. 14/249,316, entitled "PRINTED ENERGY STORAGE DEVICE," filed Apr. 9, 2014, which is incorporated herein by reference in its entirety.

In some embodiments, the separator **300** comprises a polymer **360**, such as a polymeric gel. The polymer **360** may be combined with an electrolyte **340**. A suitable polymer **360** may exhibit electrical and electrochemical stability, for example maintaining integrity and/or functionality when combined with an electrolyte **340**, during electrochemical reactions, and/or subjected to an electric potential (e.g., an electric potential existing between the electrodes **140**, **150** of the energy storage device). In some embodiments, the polymer **360** can be an inorganic polymer. In some embodiments, the polymer **360** can be a synthetic polymer. The separator **300** may include a polymer **360** comprising, for example, cellulose (e.g., cellophane), polyamide (e.g., nylon), polypropylene, polyolefin, polyethylene (e.g., radiation-grafted polyethylene), poly(vinylidene fluoride), poly(ethylene oxide), poly(acrylonitrile), poly(vinyl alcohol), poly(methyl methacrylate), poly(vinyl chloride), poly[bis(methoxy ethoxy ethoxyphosphazene)], poly(vinyl sulfone), poly(vinyl pyrrolidone), poly(propylene oxide), copolymers thereof, combinations thereof, and/or the like. In some embodiments, the polymer **360** comprises polytetrafluoroethylene (PTFE), including for example an aqueous solution comprising a dispersion of PTFE in water (e.g., a Teflon® aqueous suspension). In some embodiments, the separator **300** can comprise asbestos, potassium titanate fibers, fibrous sausage casing, borosilicate glass, zirconium oxide, combinations thereof, and/or the like. In some embodiments, the electrolyte **340** is immobilized within or on the polymer **360** to form a solid or semi-solid substance. In some such embodiments, the electrolyte **340** is immobilized on or within a polymeric gel, for example to form an electrolytic gel.

In some embodiments, the separator **300** optionally comprises an adhesive material to enable improved adherence of frustules **320** within the separator **300** and/or between the separator **300** and a first electrode **140** and/or a second electrode **150** of an energy storage device. In some embodiments, the adhesive material comprises a polymer **360**. For example, the adhesive material may comprise a polymer **360** that exhibits electrical and electrochemical stability, and provides sufficient adhesion within the separator **300** and/or between the separator **300** and a first electrode **140** and/or a second electrode **150** of an energy storage device.

In some embodiments, an ink for printing a separator of an energy storage device comprises a plurality of frustules having no or substantially no surface modifications, polymer, ionic liquid, electrolyte salt, and/or a solvent. Examples of suitable solvents are provided in U.S. patent application Ser. No. 14/249,316, entitled "PRINTED ENERGY STORAGE DEVICE," filed Apr. 9, 2014, which is incorporated herein by reference in its entirety. In some embodiments, a solvent for an ink used to print a separator can comprise dimethyl formamide (DMF), dimethyl acetamide (DMAC), tetramethyl urea, dimethyl sulfoxide (DMSO), triethyl phosphate, n-methyl-2-pyrrolidone (NMP), combinations thereof, and/or the like. In some embodiments, the ink for printing the separator comprises the following composition: about 5 weight % to about 20 weight % frustules having no surface modifications (e.g., purified frustules), about 3 weight % to about 10 weight % of the polymer component (e.g., polyvinylidene fluoride, for example Kynar® ADX commercially available from Arkema Inc. of King of Prussia, Pa.), about 15 weight % to about 40% ionic liquid (e.g., 1-ethyl-3-ethylimidazolium tetrafluoroborate), about 1 weight % to about 5% salt (e.g., zinc tetrafluoroborate), about 25 weight % to about 76 weight % solvent (e.g., N-Methyl-2-pyrrolidone). In some embodiments, other polymers, ionic liquids, salts (e.g., other zinc salt) and/or solvents may also be suitable.

In some embodiments, a process for preparing the ink for a separator can include dissolving the binder in the solvent. For example, dissolving the binder in the solvent may include heating the mixture comprising the binder and the

solvent for about 5 min to about 30 min at a temperature of about 80° C. to about 180° C. In some embodiments, the heating can be performed using a hot plate. In some embodiments, the ionic liquid and electrolyte salt can be added to the mixture, such as while the mixture is warm after being heated. The binder, solvent ionic liquid and electrolyte salt may be stirred to facilitate desired mixing, such as for about 5 min to about 10 min. In some embodiments, the frustules can be subsequently added. Addition of the frustules may be facilitated by mixing, such as by using a planetary centrifugal mixer. Mixing may be performed using the planetary centrifugal mixer for about 1 min to about 15 min.

FIG. **9** shows an example electrode layer or membrane **400** that may form part of an energy storage device (e.g., any of the energy storage devices as described with reference to FIGS. **6** and **7**A through **7**E). The electrode **400** includes frustules **420**. In some embodiments, an energy storage device includes one or more electrode layers or membranes **400** comprising frustules **420** (e.g., the first electrode **140** and/or the second electrode **150** of any of the energy storage devices as described with reference to FIGS. **6** and **7**A through **7**E). For example, an energy storage device may include an electrode layer or membrane **400** comprising a dispersion including frustules **420**. As described herein, the frustules **420** may be sorted according to a shape, dimensions, material, porosity, combinations thereof, and/or the like, such that the electrode **400** comprises frustules **420** having a uniform or substantially uniform shape, dimension (e.g., length, diameter), porosity, material, combinations thereof, and/or the like. For example, the electrode **400** may include frustules **420** having a cylindrical or substantially cylindrical shape (e.g., as shown in FIG. **9**), a spherical or substantially spherical shape, another shape, and/or combinations thereof. In some embodiments, the electrode **400** includes frustules **420** having a material and/or structures applied or formed on a surface of the frustules **420**. The electrode **400** may comprise frustules **420** comprising no or substantially no surface modifying material, and may be insulating, and/or may have surface modifying structures applied or formed on a surface of the frustules **420**. The electrode **400** may comprise frustules **420** comprising a material and/or structures applied or formed on a surface of the frustules **420** to modify a characteristic or attribute of the frustules **420** (e.g., as schematically illustrated in FIG. **9** by the chicken foot-shaped features on the surfaces of the frustules **420**). The electrode **400** may comprise some frustules **420** comprising no or substantially no surface modifying material and/or surface modifying structures applied or formed on a surface of the frustules **420** and some frustules **420** comprising a material and/or structures applied or formed on a surface of the frustules **420** to modify a characteristic or attribute of the frustules **420**.

The electrode **400** may comprise frustules **420** selected for mechanical strength such that an energy storage device including the electrode **400** may withstand compressive force and/or shape modifying deformation. In some embodiments, the electrode **400** comprises frustules **420** configured to increase efficiency of an energy storage device, for example by facilitating flow of ionic species within the electrode **400** and/or between the electrode **400** and other parts of the energy storage device. For example, frustules **420** may have a uniform or substantially uniform shape, dimension, porosity, surface modifying material and/or structures, combinations thereof, and/or the like, for improved energy storage device efficiency and/or mechanical strength. The electrode **400** of an energy storage device may comprise cylindrical or substantially cylindrical frustules **420** including walls having a desired porosity, dimensions, and/or surface modifying material and/or structures.

The electrode **400** may comprise one or more layers of frustules **420**. The electrode **400** comprising frustules **420** may have a uniform or substantially uniform thickness. In some embodiments, thickness of an electrode **400** comprising frustules **420** depends at least in part on resistance, amount of available material, desired energy device thickness, or the like. In some embodiments, thickness of an electrode **400** comprising frustules **420** is from about 1 μm to about 100 μm, including from about 1 μm to about 80 μm, from about 1 μm to about 60 μm, from about 1 μm to about 40 μm, from about 1 μm to about 20 μm, from about 1 μm to about 10 μm, from about 5 μm to about 100 μm, including from about 5 μm to about 80 μm, from about 5 μm to about 60 μm, from about 5 μm to about 40 μm, from about 5 μm to about 20 μm, from about 5 μm to about 10 μm, from about 10 μm to about 60 μm, from about 10 μm to about 40 μm, from about 10 μm to about 20 μm, from about 10 μm to about 15 μm, and from about 15 μm to about 30 μm. In some embodiments, thickness of an electrode **400** comprising frustules **420** is less than about 100 μm, less than about 90 μm, less than about 80 μm, less than about 70 μm, less than about 60 μm, less than about 50 μm, less than about 40 μm, less than about 30 μm, less than about 20 μm, less than about 10 μm, less than about 5 μm, less than about 2 μm, or less than about 1 μm, and including ranges bordering and including the foregoing values. Other thicknesses of the separator **300** are also possible.

The electrode **400** may comprise frustules **420** having a non-uniform or substantially non-uniform shape, dimension, porosity, surface modifying material and/or structure, combinations thereof, and/or the like.

In some embodiments, the electrode **400** optionally comprises a material to enhance the conductivity of electrons within the electrode **400**. For example, referring again to FIG. **9**, in some embodiments, the electrode **400** comprises electrically conductive filler **460** to improve electrical conductivity within the electrode **400**. Electrically conductive filler **460** may comprise a conductive carbon material. For example, electrically conductive filler **460** may comprise graphitic carbon, graphene, carbon nanotubes (e.g., single-wall and/or multi-wall), combinations thereof, and/or the like. In some embodiments, electrically conductive filler **460** can include a metallic material (e.g., silver (Ag), gold (Au), copper (Cu), nickel (Ni), and/or platinum (Pt)). In some embodiments, electrically conductive filler **460** can include a semiconductor material (e.g., silicon (Si), germanium (Ge)), and/or a semiconductor-containing alloy (e.g., an aluminum-silicon (AlSi) alloy). In energy storage devices **100** comprising a plurality of electrodes **400**, the electrodes **400** may include different frustules and/or different additives, for example including different ions and/or ion-producing species. In some embodiments, the electrode **400** may comprise an electrolyte, for example the electrolyte **340** described herein with respect to the separator **300** of FIG. **8**. In some embodiments, the electrode **400** may comprise a polymer, for example the polymer **360** described herein with respect to the separator **300** of FIG. **8**. In some embodiments, the electrode **400** can include one or more active materials (e.g., free active materials, such as active materials in addition to nanostructured active materials on one or more surfaces of diatom frustules).

In some embodiments, the electrode **400** can include a binder. The binder may comprise a polymer. Suitable polymers, polymeric precursors and/or polymerizable precursors, for an electrode binder, can include for example,

polyvinyl pyrrolidone (PVP), polyvinyl alcohol (PVA), polyvinylidene fluoride, polyvinylidene fluoride-trifluoroethylene, polytetrafluoroethylene, polydimethylsiloxane, polyethylene, polypropylene, polyethylene oxide, polypropylene oxide, polyethylene glycolhexafluoropropylene, polyethylene terephthalatpolyacrylonitrile, polyvinyl butyral, polyvinylcaprolactam, polyvinyl chloride; polyimide polymers and copolymers (e.g., aliphatic, aromatic and/or semi-aromatic polyimides), polyamides, polyacrylamide, acrylate and (meth)acrylate polymers and copolymers such as polymethylmethacrylate, polyacrylonitrile, acrylonitrile butadiene styrene, allylmethacrylate, polystyrene, polybutadiene, polybutylene terephthalate, polycarbonate, polychloroprene, polyethersulfone, nylon, styrene-acrylonitrile resin; polyethylene glycols, clays such as hectorite clays, garamite clays, organomodified clays; saccharides and polysaccharides such as guar gum, xanthan gum, starch, butyl rubber, agarose, pectin; celluloses and modified celluloses such as hydroxyl methylcellulose, methylcellulose, ethyl cellulose, propyl methylcellulose, methoxy cellulose, methoxy methylcellulose, methoxy propyl methylcellulose, hydroxy propyl methylcellulose, carboxy methylcellulose, hydroxy ethylcellulose, ethyl hydroxyl ethylcellulose, cellulose ether, cellulose ethyl ether, chitosan, their copolymers, combinations thereof, and/or the like.

In some embodiments, the electrode **400** can include a corrosion inhibitor and/or one or more other functional additives. In some embodiments, a corrosion inhibitor can include one or more surface active organic compounds. In some embodiments, a corrosion inhibitor can comprise glycols, silicates, mercury (Hg), cadmium (Cd), lead (Pb), gallium (Ga), indium (In), antimony (Sn), bismuth (Bi), combinations thereof, and/or the like.

In some embodiments, the electrode **400** optionally comprises an adhesive material to enable improved adhesion of frustules **420** within the electrode **400** and/or between the electrode **400** and another component of the energy storage device such as a separator **130** and/or a current collector **110**, **120**. In some embodiments, the adhesive material in the electrode **400** comprises a polymer, for example the polymer **360** described herein.

In some embodiments, an ink for printing an electrode of an energy storage device can comprise a plurality of frustules comprising nanostructures formed on one or more surfaces, a conductive filler (e.g., carbon nanotubes, graphite), a binder component, electrolyte (e.g., ionic liquid, electrolyte salt), and/or a solvent. For example, the electrolyte may have a composition as described herein. In some embodiments, one or more solvents described with reference to a separator ink may also be suitable for the ink for printing the electrode. In some embodiments, a solvent for an ink used to print an electrode can comprise dimethyl formamide (DMF), dimethyl acetamide (DMAC), tetramethyl urea, dimethyl sulfoxide (DMSO), triethyl phosphate, n-methyl-2-pyrrolidone (NMP), combinations thereof, and/or the like. In some embodiments, the ink for printing the electrode can comprise frustules having an oxide of manganese nanostructures formed on one or more surfaces. In some embodiments, the ink for printing the electrode comprises frustules having ZnO nanostructures formed on one or more surfaces.

In some embodiments, ink for printing an electrode of an energy storage comprising an oxide of manganese can have the following composition: about 10 weight % to about 20 weight % frustules having one or more surfaces covered by the oxide of manganese, about 0.2 weight % to about 2 weight % carbon nanotubes (e.g., multi-wall carbon nanotubes, for example commercially available from SouthWest NanoTechnologies of Norman, Okla.), up to about 10 weight % graphite (e.g., C65 commercially available from Timcal Graphite and Carbon, of Switzerland), about 1 weight % to about 5 weight % binder (e.g., polyvinylidene fluoride, such as HSV 900 Kynar® commercially available from Arkema Inc. of King of Prussia, Pa.), about 2 weight % to about 15 weight % ionic liquid (e.g., 1-ethyl-3-ethylimidazolium tetrafluoroborate), and about 48 weight % to about 86.8 weight % solvent (e.g., N-Methyl-2-pyrrolidone). In some embodiments, the oxide of manganese has the formula Mn_xO_y where x is about 1 to about 3 and y is about 1 to about 4. For example, the ink may be printed to form a cathode of a battery.

In some embodiments, ink for printing an electrode of an energy storage comprising ZnO can have the following composition: about 10 weight % to about 20 weight % frustules comprising ZnO nanostructures formed thereon, about 0.2 weight % to about 2 weight % carbon nanotubes (e.g., multi-wall carbon nanotubes, for example commercially available from SouthWest NanoTechnologies of Norman, Okla.), up to about 10 weight % graphite (e.g., C65 commercially available from Timcal Graphite and Carbon of Switzerland), about 1 weight % to about 5 weight % binder (e.g., polyvinylidene fluoride, such as HSV 900 Kynar® commercially available from Arkema Inc. of King of Prussia, Pa.), about 2 weight % to about 15 weight % ionic liquid (e.g., 1-ethyl-3-ethylimidazolium tetrafluoroborate), about 0.3 weight % to about 1% weight % electrolyte salt (e.g., zinc tetrafluoroborate), and about 47 weight % to about 86.5 weight % solvent (e.g., N-Methyl-2-pyrrolidone). For example, the ink may be printed to form an anode of a battery.

In some embodiments, the carbon nanotubes can comprise multi-wall and/or single wall carbon nanotubes. In some embodiments, other types of graphite, polymer binder, ionic liquid and/or solvent can also be suitable.

In some embodiments, a process for preparing the ink for printing the electrode can be configured to provide desired dispersion of carbon nanotubes in the ink, saturate the frustules with the ionic liquid (e.g., providing ionic liquid within, on interior surfaces, exterior surfaces, and/or within pores, of frustules) and/or thoroughly mix components of the ink. In some embodiments, a process of preparing the ink comprises dispersing the carbon nanotubes in the ionic liquid. In some embodiments, the carbon nanotubes can be dispersed in the ionic liquid using an automated mortar and pestle. In some embodiments, the carbon nanotubes and the ionic liquid may then be dispersed in the solvent. The carbon nanotubes and ionic liquid may be dispersed in the solvent using an ultrasonic tip. In some embodiments, the frustules comprising nanostructures formed thereon (e.g., oxide of manganese or ZnO nanostructures) and graphite may be added to the carbon nanotubes, ionic liquid, and solvent, and stirred using a centrifugal mixer. In some embodiments, the electrolyte salt can also be added to the carbon nanotubes, ionic liquid, and solvent, along with the frustules and graphite, and stirred using a centrifugal mixer. For example, the frustules, graphite, carbon nanotubes, ionic liquid, solvent, and/or electrolyte salt, may be mixed using a planetary centrifugal mixer for about 1 minutes (min) to about 10 min. In some embodiments, a solution comprising the polymer binder in the solvent can be added to the mixture comprising the frustules, graphite, carbon nanotubes, ionic liquid, solvent, and/or electrolyte salt, and heated. The solution comprising the polymer binder and the solvent can have about 10 weight % to about 20 weight % of the polymer binder. The mixture comprising the polymer binder, frustules, graphite,

carbon nanotubes, ionic liquid, solvent, and/or electrolyte salt, can be heated to a temperature of about 80° C. to about 180° C. In some embodiments, the heating can be performed for about 10 min to about 30 min. In some embodiments, a hot plate can be used for heating. In some embodiments, stirring can be performed while heating (e.g., with a mixing rod).

FIGS. **10** through **13** show electrical performances of examples of printed batteries comprising oxides of manganese (e.g., oxides having the formula Mn_xO_y where x is about 1 to about 3 and y is about 1 to about 4) cathode and a ZnO anode fabricated using processes described herein. FIG. **10** is a discharge curve graph for a printed Mn_xO_y and ZnO battery, where the cathode included a plurality of frustules comprising oxides of manganese nanostructures formed thereon and the anode included a plurality of frustules comprising ZnO nanostructures formed thereon. The battery potential expressed in Volts (V) on the y-axis and the duration of discharge expressed in hours (hrs) on the x-axis. The battery was a screen printed 1.27 centimeter (cm) by 1.27 cm square (i.e. 0.5 inch (in) by 0.5 inch square). The battery included printed current collectors, anode, cathode, and separator. The anode and cathode each had an average thickness of about 40 microns (μm). The cathode had a total weight of about 0.023 grams (g), and a weight of the oxides of manganese was about 0.01 g. The weight of active material, ZnO, in the anode was in excess.

In FIG. **10**, the battery was discharged from a fully or substantially fully charged state to the cut-off voltage of about 0.8 V. The battery was discharged at about 0.01 amperes/gram (A/g). The battery demonstrated a capacity of about 1.28 milli-ampere hour (mAh), and a capacity of about 128 milli-ampere hour/gram (mAh/g), based on the weight of the cathode active material. FIG. **11** shows the capacitance performance of the printed battery of FIG. **10** after a number charge-discharge cycles. The battery was cycled 40 times and the capacitance performance of each cycle is shown on the y-axis as a % of the initial capacitance. As shown in FIG. **11**, the capacitance performance can be improved after a number of charge-discharge cycles.

FIG. **12** is a charge-discharge curve of another example of a printed Mn_xO_y and ZnO battery, showing the potential performance of each charge-discharge cycle as a function of time during three charge-discharge cycles. The potential is shown on the y-axis in Volts (V), and time is expressed on the x-axis in hours (hrs). The printed battery was a screen printed 1.27 centimeter (cm) by 1.27 cm square (i.e. 0.5 inch (in) by 0.5 inch square). The cathode of the battery included a plurality of frustules comprising oxides of manganese nanostructures formed thereon and the anode included a plurality of frustules comprising ZnO nanostructures formed thereon. The battery included printed current collectors, anode, cathode, and separator. The anode and cathode each had an average thickness of about 40 microns (μm). The cathode had a total weight of about 0.021 grams (g), and the weight of the oxides of manganese was about 0.01 g. The weight of active material (e.g., ZnO) in the anode was in excess. The printed battery of FIG. **12** was charged and discharged at about 0.01 amperes/gram (A/g), based on the weight of active material in the cathode. FIG. **13** is a charge-discharge curve of the printed Mn_xO_y and ZnO battery of FIG. **12**, where the charge and discharge was performed at about 0.04 A/g. Both sets of curves show good repeatability for both charge and discharge, indicative that the printed Mn_xO_y/ZnO battery can be an effective rechargeable battery.

Supercapacitors Comprising Surface-Modified Diatoms

In the above, energy storage devices that derive various advantages arising from diatomaceous frustules have been described. In the following, one particular type of such energy storage devices, referred to herein and in the relevant industry as supercapacitors, are described in detail. Supercapacitors, sometimes also referred to as ultracapacitors, electric double layer capacitors (EDLC) or electrochemical capacitors, are relatively new energy storage devices whose characteristics are advantageously similar to traditional electrostatic capacitors in some aspects while being similar to traditional batteries, e.g., secondary batteries, in some other aspects.

Similar to certain batteries, supercapacitors have a cathode or a positive electrode and an anode or a negative electrode that are separated by a porous separator and an electrolyte. For example, the separator may comprise a dielectric material permeable to ions and soaked in the electrolyte. Ion transport which occurs from one electrode to the other as part of an electrochemical reaction during charge or discharge of a battery does not occur in supercapacitors.

While supercapacitors are similar to traditional electrostatic capacitors in some aspects, e.g., relatively fast charging capability, they have much higher capacitance compared to traditional electrostatic capacitors. Unlike traditional electrostatic capacitors that store energy in electrodes separated by a dielectric, supercapacitors store energy at one or both of interfaces between a cathode and an electrolyte and an anode and the electrolyte.

Capacitance values of supercapacitors may be much higher than traditional electrostatic capacitors. Some supercapacitors have lower voltage limits compared to traditional electrostatic capacitors. For example, some supercapacitors are operationally limited to about 2.5-2.8 V. Some supercapacitors may operate at voltages of 2.8 V and higher. Certain such supercapacitors may exhibit a reduced service life.

Supercapacitors generally have much higher power density than batteries because they can transport charge much faster than batteries. Supercapacitors generally have much lower internal resistance compared to batteries and, as a result, they do not generate as much heat during quick charge/discharge. Some supercapacitors can be charged and discharged millions of times, while many secondary batteries can have significantly shorter typical life cycle of 500-10000 times. Some supercapacitors have significantly lower energy density compared to batteries. Some commercial supercapacitors are more expensive (higher cost per Watt) than commercial batteries.

Because of these and other characteristics, supercapacitors are used in applications in which many rapid charge/discharge cycles may be needed rather than long term energy storage. For example, applications of larger units of supercapacitors include cars, buses, trains, cranes and elevators, to name a few, where they are used for regenerative braking, short-term energy storage or burst-mode power delivery. Applications of smaller units of supercapacitors include memory backup for static random-access memory (SRAM). Other current or future applications of supercapacitors include various consumer electronics, including mobile phones, laptops, electric cars and various other devices in which batteries are used. Because they can be recharged much faster compared to batteries, they are especially attractive for devices that can benefit from faster charge rates, e.g., minutes instead of hours that current electric vehicles or mobile phones may spend charging.

In some devices, supercapacitors are used in conjunction with batteries to take advantage of advantageous characteristics of both. In these applications, supercapacitors are used when a quick charge is needed to fill a short-term power need, whereas batteries are used to provide long-term energy. Combining the two into a hybrid energy storage device can satisfy both needs while reducing battery stress, which may in turn enable a longer service life of the battery and the supercapacitor.

Because the capacitance of supercapacitors is directly proportional to the effective surface area of the electrodes, it is desirable for the electrodes of supercapacitors to have relatively large effective surface areas. The relatively large effective surface area can be realized by utilizing electrode materials having high surface to volume ratios. As described above, because of their nanoporous structure, frustules can advantageously provide a very large effective surface area to serve as a substrate on which a surface active material of supercapacitors are formed. As described herein in the context of supercapacitors, a surface active material refers to a portion of the electrode that forms an interface with an electrolyte to substantially give rise to capacitance caused by at least one of supercapacitance mechanisms, e.g., electric double layer capacitance and/or pseudo capacitance, as described below in more detail. Nanostructures, e.g., nanoparticles or nanotubes, can additionally or alternatively provide very large surface areas for a given volume of the surface active material compared to, e.g., a thin film formed of the same material. As described herein in the context of supercapacitors, a nanostructure refers to a solid material having at least one axial dimension that is submicron, e.g., about smaller than about 1000 nm, 500 nm, 200 nm, 100 nm or a dimension that is within a range defined by any of these values.

A nanostructure can have any shape described above, e.g., a nanowire, a nanosheet, a nanotube, a nanoplate, a nanoparticle, a nanobelt, a nanodisk and a rosette shaped nanostructure. The nanostructure can also have any three dimensional geometrical shapes, e.g., a sphere, a cylinder, a cone, a spheroid, an ellipsoid, a tetrahedron, a pyramid, a prism, a cube, a cuboid, a plate, a disc and a rod to name a few. In some implementations, the nanostructure can be selected to have a particular shape based on the crystal structure of the nanostructure. As described above, the inventors have discovered inventive methods of modifying the surfaces of frustules with various surface active materials. The inventors have recognized that, by synergizing the very high effective surface area of the frustules and the very high surface-to-volume ratio of nanostructured surface active materials, supercapacitors having higher power and energy densities than existing supercapacitors can be realized. For example, by modifying surfaces of frustules with nanostructured surface active material having a large surface to volume ratio, the inventors have realized supercapacitors that benefit from the synergistic effect of the frustules and the nanostructured surface active material.

According to various embodiments, a supercapacitor comprises a pair of electrodes contacting an electrolyte. In some embodiments, the electrodes may be interposed by the electrolyte and may further comprise a separator, e.g., immersed in the electrolyte. In various embodiments, one or both of the electrodes comprise a plurality of frustules and surface active materials. The surface active materials contact the electrolyte to give rise to one or more supercapacitance mechanisms described below. In some embodiments, each of the frustules has formed thereon the surface active materials. The surface active materials may be nanostructured to take advantage of the high surface area of the frustules and/or to take advantage of the high surface to volume ratio of the surface active material, thereby giving rise to improved supercapacitance performance, including higher power and/or energy density. For example, the surface active materials may be in the form of a plurality of nanostructures covering surfaces of the frustules. The nanostructures can include one or more of zinc oxide nanostructures, manganese oxide nanostructures or carbon nanostructures. The performance of the disclosed supercapacitors benefits from the synergistic effect of the high surface area provided by the nanoporosity of the structure of diatom frustules and the high surface to volume ratio of the surface active materials. Because the surface active materials, e.g., nanostructures, are grown on diatom frustules, they are not agglomerated, and relatively larger portions of their surface area are accessible to electrolyte. Because the diatoms frustules are nanoporous, the electrolyte has direct access to the nanostructures and can easily move throughout the device. The disclosed supercapacitors can advantageously be manufactured using scalable techniques such as printing. Manufactured supercapacitors can be used as small scale devices, for example in printed electronics, and/or can be produced in large volume and folded in a shape for more powerful applications.

Without being bound to any theory, supercapacitors can store energy by different mechanisms, which include electric double-layer capacitance and/or pseudocapacitance. Double layer capacitance has electrostatic characteristics, while pseudocapacitance has electrochemical characteristics. The different mechanisms are described in more detail below. Depending on whether the storage mechanism has double-layer capacitance characteristics and/or pseudocapacitance characteristics, and depending on whether the supercapacitor has two same or symmetric electrodes or two different or asymmetric electrodes, the supercapacitor comprising one or both of the electrodes having a plurality of frustules coated with nanostructured surface active material can be configured as one of three distinct groups of supercapacitors.

A first group of supercapacitors has both electrodes configured as pseudo capacitors, where each of the electrodes comprises frustules and a transition metal oxide (e.g., manganese oxide or zinc oxide) and is configured to give rise to pseudo capacitance. For example, the frustules may have a transition metal oxide formed thereon in the form of nanostructures. A second group of supercapacitors has both electrodes configured as EDLCs, where each of the electrodes comprises frustules and carbon (e.g., carbon nanotubes) and is configured to give rise to double layer capacitance. For example, the frustules may have carbon formed thereon in the form of nanostructures. A third group of supercapacitors, which may be referred to as hybrid supercapacitors, has one of the electrodes that is configured as a EDLC and the other of the electrodes that is configured a pseudo capacitor. When included as part of a hybrid capacitor, the electrode configured as the pseudo capacitor may serve as a cathode or a positively charged electrode, and the electrode configured as the EDLC may serve as an anode or a negatively charged electrode. Without being bound to any theory, operational principles of the three groups of supercapacitors are described herein.

FIG. **14**A illustrates a cross-sectional view of a supercapacitor **1400** having both electrodes configured as a double-layer capacitor. FIG. **14**B illustrates a cross-sectional view of the supercapacitor of FIG. **14**A in operation, where a voltage is applied across the electrodes. FIGS. **14**A and **14**B illustrate the supercapacitor **1400** in a discharged state and

a charged state, respectively. The supercapacitor **1400** includes a first electrode **1440**, which may be positively charged in operation, and a second electrode **1450**, which may be negatively charged in operation. The supercapacitor **1400** optionally includes first and second current collectors **1410**, **1420** electrically coupled to the electrodes **1440**, **1450**, respectively. The first and second electrodes **1440**, **1450** are interposed by a separator **1430** and are ionically connected to each other via an electrolyte **1460** filling the gap between the first and second electrodes **1440**, **1450**. The electrolyte **1460** comprises a mixture of positive and negative ions **1470**, **1480** dissolved in a solvent. The surface of each of the two electrodes **1440**, **1450** contacts the electrolyte **1460** to form active interfaces. At the active interfaces between the electrodes **1440**, **1450**, and the electrolyte **1460**, the double layer capacitance effect arises.

Referring to FIG. **14**A, in the discharged state, the positive ions **1470** and negative ions **1480** may be dispersed randomly. In operation, referring to FIG. **14**B, applying a voltage across the first and second electrodes **1440**, **1450**, e.g., by negatively charging the second current collector **1420** relative to the first current collector **1410** and/or positively charging the first current collector **1410** relative to the second current collector **1420**, causes both electrodes **1440**, **1450** to generate electrical double layers. Each of the electrical double layers includes two layers of charge, as illustrated in FIG. **14**B. Without being bound to any theory, for example, a layer of electrostatic charge, e.g., a sheet of negative electronic charge, may form at the surface of the second electrode **1450**, e.g., at the surface of the surface active material, and an opposite layer of electrostatic charge, e.g., a sheet of positive ionic charge, may form adjacent to the surface of the electrode **1450** in the electrolyte **1460**. The two sheets of charge are separated by a layer **1490**, e.g., a monolayer, of molecules of the solvent of the electrolyte **1460**, sometimes referred to as inner Helmholtz plane (IHP). This layer **1490** of solvent molecules serves as a layer of dielectric giving rise to a first capacitance (C_{d1}) at the second electrode **1450** side. In an analogous manner, a layer **1500** of solvent molecules forms between a layer of electrostatic charge, e.g., a positive electronic charge layer at the surface of the first electrode **1440**, e.g., at the surface of the surface active material, and an opposite layer of electrostatic charge, e.g., a negative ionic charge, may form adjacent to the surface of the first electrode **1440** in the electrolyte **1460**. The layer **1500** of solvent molecules serves as another layer of dielectric giving rise to a second capacitance (C_{d2}) at the side of the first electrode **1440**.

As described herein, each of the layers **1490**, **1500** of solvent molecules formed adjacent to the first and second electrodes **1450**, **1440**, respectively, serves as a dielectric layer giving rise to the capacitances C_{d1} and C_{d2}. The capacitors formed at the second electrode **1450** and the first electrode **1440** are electrically connected in series by the electrolyte **1460** to provide a series supercapacitance Cs that can be expressed as:

$$\frac{1}{C_s} = \frac{1}{C_{d1}} + \frac{1}{C_{d2}} \quad \text{Eq. 1}$$

For a given solvent of the electrolyte **1460**, the amount of charge stored per unit voltage in an EDLC is a function of the electrode size. Similar to classical electrostatic capacitance, the capacitance of Cal arising from the first double layer capacitor on the side of the second electrode **1450** may be approximated by

$$C_{d1}=\varepsilon_{1d}d_1, \quad \text{Eq. 2}$$

where ε_1 is the permittivity of the solvent of the electrolyte **1460**, and d_1 is the effective thickness of the layer **1490** of solvent molecules formed adjacent to the second electrode **1450**. Similarly, the capacitance C_{d2} arising from the second double layer on the side of the first electrode **1440** may be approximated by

$$C_{d2}=\varepsilon_2 d_2, \quad \text{Eq. 3}$$

where ε_2 is the permittivity and d_2 is the effective thickness of the layer **1500** of solvent molecules of the electrolyte **1460** formed adjacent to the second electrode **1440**. The stored energy in each of the double-layers is approximately linear with respect to the capacitance, and corresponds to the concentration of the adsorbed ions. The energy E stored in the supercapacitor can be expressed as:

$$E = \frac{C_s A V^2}{2}, \quad \text{Eq. 4}$$

where C_s is the supercapacitor capacitance described above, A is the effective surface area of the electrodes, and V is the voltage. The power of the supercapacitor can be expressed as:

$$P_{max} = \frac{V^2}{4R}, \quad \text{Eq. 5}$$

where R is the equivalent series resistance of the supercapacitor. According to the above expressions of the capacitance, energy and power, the higher power and energy of the supercapacitors are achieved by, for a given electrolyte, increasing the surface area (A) of electrodes **1450**, **1440**, increasing the voltage (V) the supercapacitor and by decreasing the equivalent resistance (R) attributable to the electrodes, electrolytes and interfaces between the electrode materials and supercapacitor layers. The electric double-layer capacitance values are extremely high relative to traditional electrostatic capacitors with similar macroscopic electrode sizes, arising in part from the extremely thin layers **1490**, **1500** of solvent molecules, which can be as thin as a monolayer thickness, e.g., on the order of a few angstroms (0.3-0.8 nm), which can of the order of the Debye length. The active area of the electrodes are also extremely high as described above, arising from the large surface area of the frustules, whose effective surface area is further enhanced by the nanostructured active material formed thereon.

Based on the above-described mechanism of EDLC, unlike energy storage in batteries, the process of generating electric double layer capacitance does not involve a transfer of charge between the electrodes using electrolyte. While charge in conventional capacitors is transferred via electrons, capacitance in double-layer capacitors is related to the moving speed of ions through the electrolyte and through the resistive porous structure of the frustules. Since no chemical changes take place within the electrode or electrolyte, the EDLC can have much higher cycling lifetimes compared to batteries.

FIG. **15** illustrates a cross-sectional view of a supercapacitor **1500** comprising an electrode that is configured as a

pseudo capacitor. The supercapacitor **1500** may be configured in a similar manner to the supercapacitor **1400** illustrated above, except for the structure and the composition of the electrodes. While the supercapacitor **1500** includes a first electrode (not shown), which may be positively charged in operation, and a second electrode **1550**, which may be negatively charged in operation, only the second electrode **1550** illustrated as a pseudo capacitor is shown for illustration purposes. The first electrode may be configured as another pseudo capacitor, or as an EDLC described above. The surface of each of the first electrode and the second electrode **1550** contacts the electrolyte **1460**. At the contacting interface between the first electrode and the second electrode **1550** and the electrolyte **1460**, a pseudo capacitance effect arises.

Without being bound to any theory, in operation, applying a voltage across the first electrode and the second electrode **1550** moves positive and negative ions in the electrolyte **1460** in opposite directions towards the first electrode and the second electrode **1550**, where electric double layer capacitors may be formed, for example in a similar manner as described above with respect to FIGS. **14**A, **14**B. Pseudocapacitance can arise when ions in the electrolyte pervade the electric double-layer and become adsorbed on the electrode surface, as illustrated in FIG. **15**. This pseudocapacitance stores electrical energy by means of reversible Faradaic redox reactions on the surface the electrode of a supercapacitor forming an electric double layer described above. Unlike the electric double layer capacitance effect, the pseudocapacitance is accompanied with an electron charge-transfer between the electrolyte **1460** and the adsorbed ions. This Faradaic charge transfer originates by a very fast sequence of reversible redox, intercalation or electrosorption processes. The ability of electrodes to exhibit pseudocapacitance depends on the chemical affinity of electrode materials to the ions adsorbed on the electrode surface as well as on the structure and the structure of the electrode. Materials exhibiting redox behavior for use as electrodes in pseudo capacitors include transition-metal oxides. The pseudo capacitance can be expressed as the amount of charge (q) stored per applied potential (V), or

$$C=dq/dV. \quad \text{Eq. 6}$$

Similar to double layer capacitance, pseudo capacitance or electrochemical capacitance arises at the surface of the electrode, e.g., at the surface of surface active materials formed on the frustules. As a result, the specific surface area is directly proportional to the number of active sites for the redox reactions, and hence the magnitude of pseudocapacitance. This Faradaic energy storage with fast redox reactions makes charging and discharging much faster than batteries.

Faradaic pseudo capacitance arises in conjunction with static double-layer capacitance. Depending on the circumstance, its magnitude may exceed the value of double-layer capacitance for the same surface area by orders of magnitude, depending on the nature and the structure of the electrode.

In the following, various aspects of the supercapacitor are disclosed. While it may not be described in detail, the frustules according to various embodiments may have any structure and may be prepared using any method described throughout the application, including without limitation, FIGS. **1**-**5**X and the associated text. Various nanostructures including zinc oxide, manganese oxide and carbon nanostructures according to various embodiments may have any structure including, e.g., FIG. **5** and may be prepared using any method described throughout the application, including without limitation, FIGS. **1**-**5**X and the associated text.

Supercapacitor Electrodes Comprising Frustules Having Formed Thereon Active Materials

As described above, the interface between the surface active material of the electrode and the electrolyte provide sites for energy storage. In the following, various surface active materials configured to give rise to pseudo capacitance are described. As described, the surface active material can form a coating on the frustules, e.g., on the surfaces of the frustules. The coating may be in the form of nanostructured surface active material, which may be formed as part of one or more electrodes of the supercapacitor according to any relevant method, for example described elsewhere herein.

According to some embodiments, the nanostructured surface active material formed on frustule surfaces comprises one or more metal oxides, including, for example, zinc oxide (ZnO), manganese dioxide (MnO_2), manganese(II, III) oxide (Mn_3O_4), manganese(II) oxide (MnO), manganese (III) oxide (Mn_2O_3), mercury oxide (HgO), cadmium oxide (CdO), silver(I,III) oxide (AgO), silver(I) oxide (Ag_2O), nickel oxide (NiO), lead(II) oxide (PbO), lead(II, IV) oxide (Pb_2O_3), lead dioxide (PbO_2), vanadium(V) oxide (V_2O_5), copper oxide (CuO), molybdenum trioxide (MoO_3), iron (III) oxide (Fe_2O_3), iron(II) oxide (FeO), iron(II, III) oxide (Fe_3O_4), rubidium(IV) oxide (RuO_2), titanium dioxide (TiO_2), iridium(IV) oxide (IrO_2), cobalt(II, III) oxide (Co_3O_4), tin dioxide (SnO_2), niobium oxide (Nb_2O_5), combinations thereof, and the like.

According to some embodiments, the nanostructured surface active material formed on frustule surfaces comprises one or more metal-containing compounds, including, for example, manganese(III) oxohydroxide (MnOOH), nickel oxyhydroxide (NiOOH), silver nickel oxide ($AgNiO_2$), lead (II) sulfide (PbS), silver lead oxide ($Ag_5Pb_2O_6$), bismuth(III) oxide (Bi_2O_3), silver bismuth oxide ($AgBiO_3$), silver vanadium oxide (AgV_2O_5), copper(I) sulfide (CuS), iron disulfide (FeS_2), iron sulfide (FeS), lead(II) iodide (PbI_2), nickel sulfide (Ni_3S_2), silver chloride (AgCl), silver chromium oxide or silver chromate (Ag_2CrO_4), copper(II) oxide phosphate ($Cu_4O(PO_4)_2$), lithium cobalt oxide ($LiCoO_2$), metal hydride alloys (e.g., LaCePrNdNiCoMnAl), lithium iron phosphate ($LiFePO_4$ or LFP), lithium permanganate ($LiMn_2O_4$), lithium manganese dioxide ($LiMnO_2$), Li(NiMnCo)O_2, Li(NiCoAl)O_2, cobalt oxyhydroxide (CoOOH), titanium nitride (TiN), combinations thereof, and the like.

According to some embodiments, the nanostructured surface active material formed on frustule surfaces comprises mixed transition metal spinels and binary metal oxides, including, for example, $MnFe_2O_4$, $NiCo_2O_4$, $CuCo_2O_4$, $ZnCo_2O_4$, Zn_2SNO_4, $NiMoO_4$, combinations thereof, and the like.

According to some embodiments, the nanostructured surface active material formed on frustule surfaces comprises metal hydroxides, including, for example, $Ni(OH)_2$, $Co(OH)_2$, $H_2Ti_3O_7$, combinations thereof, and the like.

According to other embodiments, the nanostructured surface active material formed on frustule surfaces comprises a mixture of any of the above materials. By way of example, combinations of material that can coat the frustules include, for example, $MnxO_y$—Co_xO_y, MnO_2—NiO/$Ni(OH)_2$, Mn_xO_y—TiO_2 and Mn_xO_y—ZnO, to name a few.

In addition to the surface active material that forms the interface with the electrolyte to provide sites for energy storage, the electrode of supercapacitors also includes electrically conducting materials. In addition to providing elec-

trical conductivity to the frustules, which may be electrically insulating, to enable the electric double layer capacitance or the pseudo capacitance described above, the electrically conducting material may lower the internal resistance, for higher power, as described above. One or more of the above compounds can be coated on the frustules with one or more electrically conducting materials. The electrically conducting material may be carbon-based in some implementations. For example, the electrically conducting material may comprise one or more of various carbon compounds, e.g., graphene, graphite, carbon nanotubes (CNTs), fullerenes, carbon nanofibers and/or carbon aerogels, to name a few.

The electrically conducting material may be metal-based in some implementations. For example, the electrically conducting material may comprise a metallic element or compound, e.g., Ag, Au, stainless steel, Mn, Cu, Ni and/or Al to name a few. In some implementations, the electrically conducting material may comprise a conducting polymer, e.g., polyaniline (PANI), poly(3,4-ethylenedioxythiophene) (PEDOT), polypyrrole and/or related polymers, to name a few.

While various embodiments are described in which the surface active material and the electrically conducting material may be formed on surfaces of each of the frustules, not all embodiments necessarily include such features. In some embodiments, herein and throughout the entire application, the surface active material and the electrically conducting material may be formed, in addition to or in lieu of being formed on the surfaces of each of the frustules, on or over a layer of frustules or between the frustules within a layer of frustules.

While various embodiments are described in which the active material is nanostructured, not all embodiments necessarily include such features. In some embodiments, herein and throughout the entire application, the surface active material may form a continuous or contiguous network of a thin film of the surface active material.

Supercapacitor Electrodes Comprising Frustules Having Formed Thereon Manganese Oxide as Surface Active Material

An surface active material for a supercapacitor electrode, e.g., an electrode configured to give rise to pseudo capacitance, may include one or more manganese-containing compounds, e.g., a manganese oxide, described above. The manganese-containing compound may have a composition and be prepared using any relevant method, for example as described herein. According to some embodiments, one or more electrodes comprise frustules having formed thereon a manganese oxide (Mn_xO_y), e.g., manganese oxide nanostructures, as the surface active material. In some embodiments, the frustules have surfaces that are coated with manganese oxide nanostructures in any manner described herein. Frustules coated with manganese oxide, e.g., manganese oxide nanoparticles, may constitute about 50-95 wt. %, 55-85 wt. %, 60-80 wt. %, 65-75 wt. %, or a value in a range defined by any of these values, for instance about 70 wt. %, on the basis of the total weight of the electrode, e.g., as printed and dried.

The one or more electrodes comprising manganese oxide can additionally comprise an electrically conducting material as described above. The electrically conducting material can include, e.g., conductive carbon in the amount of about 0.1-15 wt. %, 1-13 wt. %, 3-11 wt. %, 5-9 wt. %, 6-8 wt. %, for instance about 7 wt. %, on the basis of the total weight of the electrode, e.g., as printed and dried. The conductive carbon forms part of the electrode to provide electrical conductivity as described above. The conductive carbon can improve printability of inks. The conductive carbon can increase flexibility of the resulting supercapacitor. One example of conductive carbon that can be included as part of the one or more electrodes is Timcal Super 65®, sold by Timcal Graphite & Carbon (Switzerland).

The one or more electrodes comprising manganese oxide can additionally comprise carbon nanotubes in the amount of about 0.1-15 wt. %, 1-13 wt. %, 3-11 wt. %, 5-9 wt. %, 6-8 wt. %, for instance about 7 wt. %, on the basis of the total weight of the electrode, e.g., as printed and dried. The carbon nanotubes serve as part of the electrode to provide electrical conductivity. The carbon nanotubes can improve printability of inks. The carbon nanotubes can increase flexibility of the resulting supercapacitor. One example of carbon nanotubes that can be included as part of the one or more electrodes is multiwalled carbon nanotubes, sold by Cheap Tubes Inc. (United States).

The one or more electrodes comprising manganese oxide can additionally comprise a polymer binder in the amount of about 0.1-15 wt. %, 0.5-12 wt. %, 1-9 wt. %, 2-6 wt. %, 3-5 wt. %, for instance about 4 wt. %, on the basis of the total weight of the electrode, e.g., as printed and dried. The polymer binder promotes adhesion to substrates and other layers and integrity of the layers (e.g., hold particles together). One example of polymer binder that can be included as part of the one or more electrodes is polyvinylidene fluoride (PVDF), sold by Solef 5130 (Belgium).

[0469] The one or more electrodes comprising manganese oxide can additionally comprise an electrolyte comprising an ionic liquid. The ionic liquid may be present in the amount of about 5-30 wt. %, 8-27 wt. %, 11-24 wt. %, 14-21 wt. %, 17-20 wt. %, for instance about 18 wt. %, on the basis of the total weight of the electrode, e.g., as printed and dried. The ionic liquid can serve as an electrolyte or be part of an electrolyte. One example of ionic liquid that can be included as part of the one or more electrodes is 1-ethyl-3-methylimidazolium tetrafluoroborate (C_2mimBF_4), sold by IoLitec (Germany).

The one or more electrodes comprising manganese oxide can additionally comprise a salt, which may be dissolved in the solvent or the ionic liquid in the amount of about 0.1-5 wt. %, 1-5 wt. %, 1.5-4.5 wt. %, 2.0-4.0 wt. %, 2.5-3.5 wt. %, for instance about 3 wt. %, on the basis of the total weight of the electrode, e.g., as printed and dried. The salt serves as an additive to improve ionic conductivity. The salt can promote higher capacitance by contributing to interface structure. One example of ionic liquid that can be included as part of the one or more electrodes is 1-ethyl-3-methylimidazolium tetrafluoroborate (C_2mimBF_4), sold by IoLitec (Germany). The salt and the ionic liquid that can be included as part of the one or more electrodes can be any salt or any ionic liquid described herein.

In some embodiments, in addition to an ionic liquid or a combination of an ionic liquid and a salt, the one or more electrodes comprising manganese oxide may comprise a solvent of the electrolyte that may be residual after drying.

In some embodiments, the one or more electrodes comprise a gel that serves as a medium for ion transportation. The gel can include the electrolyte, which can include one or more of a solvent, salt and an ionic liquid, and a suitable gel-forming or a gelling polymer, as described herein.

In some embodiments, the gel can at least partially fill the network of pores in the frustules. When the gel substantially entirely fills the network of pores, the resulting electrode may be substantially free of pores comprising voids. On the other hand, when the gel partially fills the network of pores,

the resulting separator may still include some pores comprising voids. The voids, when present, may be filled with the electrolyte.

In some configurations, once it fills the network of pores in the frustules, the gel including the electrolyte may remain relatively localized without freely moving through the network of pores in the frustules.

Supercapacitor Electrodes Comprising Frustules and Zine Oxide as Surface Active Material

An active material for a supercapacitor electrode, e.g., an electrode configured to give rise to pseudo capacitance, includes one or more zinc-containing compounds, e.g., a zinc oxide, described above. The zinc-containing compound may have a composition and be prepared using any relevant method described herein. According to some embodiments, one or more electrodes comprise frustules having formed thereon a zinc oxide (Zn_xO_y, e.g., ZnO), e.g., zinc oxide nanostructures, as the surface active material. In some embodiments, the frustules have surfaces that are coated with zinc oxide nanostructures in any manner described herein. Frustules coated with zinc oxide, e.g., zinc oxide nanoparticles, can constitute about 25-90 wt. %, 30-80 wt. %, 35-70 wt. %, 40-60 wt. %, 45-50 wt. % or a value in a range defined by any of these values, for instance about 46 wt. %, on the basis of the total weight of the electrode, e.g., as printed and dried.

The one or more electrodes comprising zinc oxide can additionally comprise an electrically conducting material as described above. The electrically conducting material can include, e.g., conductive carbon in the amount of about 0.1-15 wt. %, 2-14 wt. %, 4-13 wt. %, 6-12 wt. %, 8-11 wt. %, for instance about 10 wt. %, on the basis of the total weight of the electrode, e.g., as printed and dried. The conductive carbon can form part of the electrode to provide electrical conductivity. The conductive carbon can improve printability of inks. The conductive carbon can increase flexibility of the resulting supercapacitor. The conductive carbon can serve as part of the electrode to provide electrical conductivity as described above. The conductive carbon can improve printability of inks. The conductive carbon can increase flexibility of the resulting supercapacitor. One example of conductive carbon that can be included as part of the one or more electrodes is Timcal Super 65®, sold by Timcal Graphite & Carbon (Switzerland).

The one or more electrodes comprising zinc oxide can additionally comprise carbon nanotubes in the amount of about 0.1-15 wt. %, 0.1-11 wt. %, 0.1-7 wt. %, 0.1-5 wt. %, 1-3 wt. %, for instance about 2 wt. %, on the basis of the total weight of the electrode, e.g., as printed and dried. The carbon nanotubes can serve as part of the electrode to provide electrical conductivity. The carbon nanotubes can improve printability of inks. The carbon nanotubes can increase flexibility of the resulting supercapacitor. One example of carbon nanotubes that can be included as part of the one or more electrodes is multi-walled carbon nanotubes, sold by Cheap Tubes Inc. (United States).

The one or more electrodes comprising zinc oxide can additionally comprise a polymer binder in the amount of about 0.1-15 wt. %, 0.5-13 wt. %, 1-11 wt. %, 2-9 wt. %, 3-7 wt. %, for instance about 5 wt. %, on the basis of the total weight of the electrode, e.g., as printed and dried. The polymer binder can promote adhesion to substrates and other layers and integrity of the layers (e.g., hold particles together). One example of polymer binder that can be included as part of the one or more electrodes is polyvinylidene fluoride (PVDF), sold by Solef 5130 (Belgium).

The one or more electrodes comprising zinc oxide can additionally comprise an electrolyte comprising an ionic liquid. The ionic liquid may be present in the amount of about 10-50 wt. %, 15-50 wt. %, 20-45 wt. %, 25-40 wt. %, 30-35 wt. %, for instance about 34 wt. %, on the basis of the total weight of the electrode, e.g., as printed and dried. The ionic liquid can serve as an electrolyte or be part of an electrolyte. One example of ionic liquids that can be included as part of the one or more electrodes is 1-ethyl-3-methylimidazolium tetrafluoroborate (C_2mimBF_4), sold by IoLitec (Germany).

The one or more electrodes comprising zinc oxide can additionally comprise a salt, which may be dissolved in the ionic liquid in the amount of about 0.1-5 wt. %, 1-5 wt. %, 1.5-4.5 wt. %, 2.0-4.0 wt. %, 2.5-3.5 wt. %, for instance about 3 wt. %, on the basis of the total weight of the electrode, e.g., as printed and dried. The salt can serve as an additive to improve ionic conductivity. The salt can promote higher capacitance by contributing to interface structure. One example of ionic liquids that can be included as part of the one or more electrodes is 1-ethyl-3-methylimidazolium tetrafluoroborate (C_2mimBF_4), sold by IoLitec (Germany).

In some embodiments, in addition to an ionic liquid or a combination of an ionic liquid and a salt, the one or more electrodes comprising zinc oxide may comprise a solvent of the electrolyte that may be residual after drying.

Supercapacitor Electrodes Comprising Frustules Having Formed Thereon Carbon Nanostructures as Surface Active Material

An active material for a supercapacitor electrode, e.g., an electrode configured to give rise to EDCL, includes one or more carbon nanostructures, e.g., CNT as described above. The carbon nanostructures may have a composition and be prepared using any relevant method described herein. According to some embodiments, one or more electrodes comprise frustules having formed thereon carbon structures, e.g., carbon nanostructures, as the surface active material. In some embodiments, the frustules have surfaces that are coated with carbon nanostructures, e.g., CNTs, in any manner described above. The one or more electrodes comprise CNTs in the amount of about 1-50 wt. %, 1-40 wt. %, 1-30 wt. %, 1-20 wt. %, 5-15 wt. %, for instance about 11 wt. %, on the basis of the total weight of the electrode, e.g., as printed and dried. The carbon nanotubes can serve as part of the surface active material. The carbon nanotubes can provide printability of inks. The carbon nanotubes can increase flexibility of the resulting supercapacitor. One example of carbon nanotubes that can be included as part of the one or more electrodes is multiwall carbon nanotubes, sold by Cheap Tubes Inc. (United States).

The one or more electrodes comprising carbon can additionally comprise an electrically conducting material as described above. The electrically conducting material can include, e.g., conductive carbon in the amount of about 1-50 wt. %, 1-40 wt. %, 1-30 wt. %, 1-20 wt. %, 5-15 wt. %, for instance about 11 wt. %, on the basis of the total weight of the electrode, e.g., as printed and dried. The conductive carbon can form part of the surface active material. The conductive carbon can provide printability of inks. The conductive carbon can increase flexibility of the resulting supercapacitor. One example of conductive carbon that can be included as part of the one or more electrodes is Timcal Super 65®, sold by Timcal Graphite & Carbon (Switzerland).

The one or more electrodes comprising CNTs can additionally comprise polymer binder in the amount of about 0.1-15 wt. %, 1-13 wt. %, 3-11 wt. %, 5-9 wt. %, for instance

about 7 wt. %, on the basis of the total weight of the electrode, e.g., as printed and dried. The polymer binder can promote adhesion to substrates and other layers and integrity of the layers (e.g., hold particles together). One example of polymer binder that can be included as part of the one or more electrodes is polyvinylidene fluoride (PVDF), sold by Solef 5130 (Belgium).

The one or more electrodes comprising CNTs can additionally comprise ionic liquid in the amount of about 10-90 wt. %, 30-85 wt. %, 50-80 wt. %, 70-75 wt. %, for instance about 71 wt. %, on the basis of the total weight of the electrode, e.g., as printed and dried. The ionic liquid can serve as an electrolyte or be part of an electrolyte. One example of ionic liquids that can be included as part of the one or more electrodes is 1-ethyl-3-methylimidazolium tetrafluoroborate (C_2mimBF_4), sold by IoLitec (Germany).

The one or more electrodes comprising CNTs can additionally comprise a salt, which may be dissolved in the ionic liquid in the amount of about 0.1-5 wt. %, 1-5 wt. %, 1.5-4.5 wt. %, 2.0-4.0 wt. %, 2.5-3.5 wt. %, for instance about 3 wt. %, on the basis of the total weight of the electrode, e.g., as printed and dried. The salt can serve as an additive to improve ionic conductivity. The salt can promote higher capacitance by contributing to interface structure. One example of ionic liquids that can be included as part of the one or more electrodes is 1-ethyl-3-methylimidazolium tetrafluoroborate (C_2mimBF_4), sold by IoLitec (Germany). The salt and the ionic liquid that can be included as part of the one or more electrodes can be any salt or any ionic liquid described herein.

In some embodiments, in addition to an ionic liquid or a combination of an ionic liquid and a salt, the one or more electrodes comprising CNT may comprise a solvent of the electrolyte that may be residual after drying.

Supercapacitor Separators

According to various embodiments, supercapacitors further comprise a separator. The separator, which may be interposed between the electrodes, can inhibit or prevent an electrical short that may result from a direct contact between the electrodes. The separator may include frustules. The separator may be configured to serve as a permeable membrane for ion transportation. Frustule-containing separators can provide lower electrical resistance, chemical stability and/or relatively small thickness. The frustules serve as a separator filler material and to improve printability, e.g., by inhibiting or preventing holes from forming during printing, thereby shorting the electrodes.

Frustule-containing separators can have any structure and composition, and can be prepared using any method described herein.

Referring to FIGS. **14**A, **14**B and **15**, each of the supercapacitors **1400**, **1500** comprises a separator **1430** comprising frustules, e.g., purified frustules that constitute about 10-70 wt. %, 13-55 wt. %, 16-45 wt. %, 19-35 wt. %, 20-25 wt. % or a value in a range defined by any of these values, for instance about 22 wt. %, on the basis of the total weight of the separator, e.g., as printed and dried. Various characteristics and processes of forming purified frustules and a separator therefrom are described above.

The separator **1430** comprising frustules can additionally comprise a thermally conductive additive in the amount of about 0.1-5 wt. %, 0.5-4 wt. %, 1-3 wt. %, 1.5-2.5 wt. %, for instance about 2 wt. %, on the basis of the total weight of the separator, e.g., as printed and dried. The thermally conductive additive may serve as a separator filler. The thermally conductive additive may serve as a heat absorbing and/or conducting agent, e.g., as a near infrared radiation (NIR) absorbing agent. As described herein, a NIR radiation may have a wavelength of 0.7 μm to 2.5 mm. The thermally conducive additive may efficiently absorb and/or conduct heat during fabrication, e.g., during a drying process using near infrared radiation (NIR). The thermally conductive additive may reduce the internal resistance of the supercapacitor, thereby improving the power. The thermally conductive additive may, e.g., be a good heat absorber, a good thermal conductor and a relatively good electrical insulator. One example of such thermally conductive additives that can be included as part of the separator is graphene oxide (GO), sold by Cheap Tubes Inc. (U.S.A). The inventors have found that, when graphene oxide is added to the ink for printing the separator, the resulting ink showed improved printability, superior heat conduction during drying (which reduces drying time) and relatively lower internal resistance of the supercapacitor, although not all such advantages are necessary. In addition, because the thermally conductive additive such as GO can be a good electrical insulator, the separator advantageously maintains the electrically insulating characteristics. In some embodiments, GO comprises sheets of GO that contact each other to form a network of contiguous GO sheets. The inventors have found, when included as part of a printed layer such as a printed separator layer, GO may reduce the drying time by as much as one order of magnitude, e.g., from tens or minutes to tens of seconds.

The separator comprising frustules can additionally comprise a polymer binder in the amount of about 5-20 wt. %, 5-15 wt. %, 5-10 wt. %, 6-8 wt. %, for instance about 7 wt. %, on the basis of the total weight of the separator, e.g., as printed and dried. The polymer binder can promotes adhesion to substrates and other layers and integrity of the layers (e.g., hold particles together). One example of polymer binder that can be included as part of the separator is polyvinylidene fluoride (PVDF), sold by Solef 5130 (Belgium).

The separator comprising frustules can additionally comprise a gelling polymer in the amount of about 0.5-10 wt. %, 1.0-7.0 wt. %, 1.5-5.0 wt. %, 2.0-4.0 wt. %, for instance about 3 wt. %, on the basis of the total weight of the separator, e.g., as printed and dried. The gelling polymer may form a gel with an ionic liquid. One example of the gelling polymer that can be included as part of the separator is polyethylene glycol, sold by Sigma Aldrich (U.S.A.).

In some embodiments, the gelling polymer forms gel that serves as a medium for ion transportation. The gel can fill the network of pores in the frustules. The gel can include the electrolyte, which can include one or more of a solvent, salt and an ionic liquid, and a suitable gel-forming or a gelling polymer, as described herein.

In some embodiments, the gel can at least partially fill the network of pores in the frustules. When the gel substantially entirely fills the network of pores, the resulting separator may be substantially free of pores comprising voids. Advantageously, the separator that is substantially free of pores can be effective in preventing undesirable movement of particles therethrough, which may be particularly advantageous in the context of printed layers having various components, e.g., frustules and/or nanostructures, that can become loose and separated.

On the other hand, when the gel partially fills the network of pores, the resulting separator may still include some pores comprising voids, which may be filled with electrolyte. Advantageously, such configuration may increase ionic conductivity for higher power.

In some configurations, once it fills the network of pores in the frustules, the gel including the electrolyte may remain relatively localized without freely moving through the network of pores in the frustules.

The separator comprising frustules can additionally comprise an electrolyte, which may include an ionic liquid. The ionic liquid may be present in the amount of about 10-80 wt. %, 30-75 wt. %, 50-70 wt. %, 55-65 wt. %, for instance about 60 wt. %, on the basis of the total weight of the separator, e.g., as printed and dried. The ionic liquid can serve as an electrolyte or be part of an electrolyte. One example of ionic liquid that can be included as part of the separator is 1-ethyl-3-methylimidazolium tetrafluoroborate (C_2mimBF_4), sold by IoLitec (Germany).

The separator comprising frustules can additionally comprise a salt, which may be dissolved in the electrolyte, in the amount of about 0.1-8 wt. %, 1-7.5 wt. %, 3.0-7.0 wt. %, 5.0-6.5 wt. %, 5.5-6.5 wt. %, for instance about 6 wt. %, on the basis of the total weight of the separator, e.g., as printed and dried. The salt can serve as an additive to improve ionic conductivity. The salt can promote higher capacitance by contributing to interface structure. One example of the salt that can be included as part of the one or more electrodes is zinc tetrafluoroborate $Zn(BF_4)_2$, sold by Sigma Aldrich (U.S.A).

As described above, various components including one or more of the electrodes and the separator of the supercapacitor may advantageously be printed using a ink. In the following, compositions of inks that can be used to print the one or more of the electrodes and the separator are described.

Advantageously, when printed, the thicknesses of each of the electrodes and the separator can be made extremely thin. Each of the separator and the electrodes can have a thickness of 10-50 microns, 50-100 microns, 100-200 microns, 200-300 microns, 300-400 microns, 400-500 microns, or a thickness in a range defined by any of these values.

Composition and Method of Preparing Printable Manganese Oxide-Containing Ink for Supercapacitor Electrodes

As described above, one of the possible advantages of the supercapacitors described herein includes the relative ease and lower cost of manufacturing, arising from printability of one or more layers of the supercapacitors, including the electrodes. According to various embodiments, a manganese oxide-containing ink that can be used to form one or more electrodes of the supercapacitor can include any component or composition, and may be prepared using any method of preparing Mn_xO_y-based inks described elsewhere herein. In some embodiments, prior to printing and drying, the manganese oxide-containing ink includes various components of the manganese oxide-containing electrode described above in the amount of about 20-70 wt. %, 25-60 wt. %, 30-50 wt. %, 30-40 wt. %, or a value in a range defined by any of these values, for instance about 34 wt. %, on the basis of the total weight of the manganese oxide-containing ink.

Prior to printing and drying, the manganese oxide-containing ink includes a solvent, which may constitute the balance of the manganese oxide-containing ink. The manganese oxide-containing ink includes the solvent in the amount of about 30-80 wt. %, 40-75 wt. %, 50-70 wt. %, 60-70 wt. %, or a value in a range defined by any of these values, for instance about 66 wt. %, on the basis of the total weight of the manganese oxide-containing ink. One example solvent is n-methylpyrrolidone.

The manganese oxide-containing ink may be prepared according to the following example method. A solvent, an ionic liquid and carbon nanotubes (CNTs) are mixed, e.g., in a vial, and the resulting mixture may be sonicated, e.g., for 1-15 min., to disperse the CNTs. The manganese oxide-coated frustules are added, and the mixture may be stirred, e.g., for 5-30 min. at 50-150° C. on a hot plate. The mixture may be further mixed in a planetary centrifugal mixer (for example, THINKY, USA) for 1-10 min. at 500-2000 rpm. Conductive carbon can be added and mixed next, followed by lab egg mixing for 1-15 min. at 150° C. Subsequently, a polymer, which may be dissolved in or mixed with a solvent, can be added, and the mixture can be stirred with lab egg stirrer with heat for 5-30 min. on a hot plate at 50-150° C. The mixture can be further mixed, e.g., on a hot plate and/or on a planetary centrifugal mixer for 1-15 min. at 500-2000 rpm.

Composition and Method of Preparing Printable Zinc Oxide-Containing Ink for Supercapacitor Electrodes

According to various embodiments, a zinc oxide-containing ink that can be used to form one or more electrodes of the supercapacitor can include any component or composition, and be prepared using any method of preparing ZnO-based inks described herein. In some embodiments, prior to printing and drying, the zinc oxide-containing ink includes various components of the zinc oxide-containing electrode described above in the amount of about 20-70 wt. %, 25-60 wt. %, 25-50 wt. %, 25-40 wt. %, or a value in a range defined by any of these values, for instance about 29 wt. %, on the basis of the total weight of the zinc oxide-containing ink.

Prior to printing and drying, the zinc oxide-containing ink includes a solvent, which may constitute the balance of the zinc oxide-containing ink. The zinc oxide-containing ink can include the solvent in the amount, of about 30-80 wt. %, 40-75 wt. %, 50-75 wt. %, 60-75 wt. %, or a value in a range defined by any of these values, for instance about 71 wt. %, on the basis of the total weight of the zinc oxide-containing ink. One example of a solvent includes n-methylpyrrolidone.

The zinc oxide-containing ink may be prepared according to the following example method. A solvent, an ionic liquid and carbon nanotubes (CNTs) are mixed, e.g., in a vial, and the resulting mixture may be sonicated, e.g., for 1-15 min., to disperse the CNTs. The zinc oxide-coated diatoms are added and the mixture is stirred, e.g., for 1-15 min. at 50-150° C. on a hot plate, and mixed, e.g., on a planetary centrifugal mixer for 1-15 min. at 500-2000 rpm. Conductive carbon can be added and mixed next, for 1-15 min. on the hotplate at 50-150° C. Subsequently, a polymer, which may be dissolved in or mixed with a solvent, can be added, and the mixture is stirred for 1-15 min. at 50-150° C. The mixture can be further mixed, e.g., on a hot plate and/or on a planetary centrifugal mixer for 1-15 min. at 500-2000 rpm.

Composition and Method of Preparing Printable Carbon Nanotube-Containing Ink for Supercapacitor Electrodes

According to various embodiments, a carbon nanotube (CNT)-containing ink that can be used to form one or more electrodes of the supercapacitor can include any component or composition, and be prepared using any method of preparing CNT-based inks described herein. In some embodiments, prior to printing and drying, the CNT-containing ink can include various components of the CNT-containing electrode described above in the amount of about 10-80 wt. %, 10-60 wt. %, 10-40 wt. %, 10-30 wt. %, or a value in a range defined by any of these values, for instance about 18 wt. %, on the basis of the total weight of the CNT-containing ink.

Prior to printing and drying, the CNT-containing ink can include a solvent, which may constitute the balance of the CNT-containing ink. The CNT-containing ink can include

the solvent in the amount of about 10-80 wt. %, 10-60 wt. %, 10-40 wt. %, 10-30 wt. %, or a value in a range defined by any of these values, for instance about 18 wt. %, on the basis of the total weight of the CNT-containing ink. One example of a solvent includes n-methylpyrrolidone.

The CNT-containing ink may be prepared according to the following one example method. Solvent, ionic liquid and CNTs are mixed together, e.g., in a vial. The resulting mixture may be sonicated for 1-15 min. to disperse the CNTs. Conductive carbon may subsequently be added and mixed, e.g., for 1-15 min. on the hotplate at 50-150° C. Subsequently, a polymer, which may be dissolved in or mixed with a solvent, may be added and the mixture may be stirred, e.g., for 1-15 min at 50-150° C. on a hot plate. The mixture can be further mixed on a planetary centrifugal mixer for 1-15 min. at 500-2000 rpm.

Composition and Method of Preparing Printable Frustule-Containing Ink for Supercapacitor Separators

According to various embodiments, a frustule-containing ink that can be used to form a separator of the supercapacitor can include any component or composition, and can be prepared using any method of preparing frustule-based inks described herein. In some embodiments, prior to printing and drying, the frustule-containing ink includes various components of the frustule-containing electrode described above in the amount of about 20-80 wt. %, 30-70 wt. %, 40-60 wt. %, 50-60 wt. %, or a value in a range defined by any of these values, for instance about 54 wt. %, on the basis of the total weight of the frustule-containing ink.

Prior to printing and drying, the frustule-containing ink includes a solvent, which may constitute the balance of the frustule-containing ink. The frustule-containing ink can include the solvent in the amount, of about 20-80 wt. %, 30-70 wt. %, 40-60 wt. %, 40-50 wt. %, or a value in a range defined by any of these values, for instance about 46 wt. %, on the basis of the total weight of the frustule-containing ink. One example solvent is tetramethyl urea.

The frustule-containing ink may be prepared according to the following example method. A gelling polymer and a binder polymer are dissolved in a solvent, e.g., at 50-150° C. on a hot plate. Graphene oxide may be mixed with an electrolyte and a solvent. The graphene oxide mixture may be sonicated for 1-15 min. and mixed with the dissolved polymers. Subsequently, the purified diatoms are added and the mixture may be stirred at 50-150° C. on the hot plate for 5-60 min.

Example Components of Printable Inks for Supercapacitor Electrodes and/or Separators

Printable inks for printing one or more layers of a supercapacitor, e.g., electrode and/or separator layers, can include purified diatom frustules, which may have any structure and composition and be prepared using any method as described herein. According to some embodiments, the purified diatom frustules may be substantially unmodified (e.g., the chemical composition of purified diatom frustules may have substantially the same composition as the frustules in natural form).

Printable inks for printing one or more electrode layers, e.g., electrode layers configured as a pseudo capacitor, can comprise diatom frustules coated with a zinc oxide (ZnO), diatom frustules coated with a manganese oxide (Mn_xO_y including, e.g., MnO, Mn_2O_3, Mn_3O_4, MnOOH and MnO_2 and their mixtures), which may have any component, composition and be prepared using any method as described herein.

Printable inks for printing one or more electrode layers, e.g., electrode layers configured as a pseudo capacitor or as an EDLC, can comprise diatom frustules coated with carbon nanotubes (CNTs), which may include any component or composition, and be prepared using any preparation method described herein. For example, CNTs included in the inks may include one or more of any of a variety of forms of CNTs, including multi wall, single wall, double wall, metallic and semiconducting, among other forms of CNTs.

Printable inks for printing one or more electrode layers, e.g., electrode layers configured as a pseudo capacitor or as an EDLC, can comprise one or more conductive carbon, which may include any component or composition and be prepared using any preparation method described herein. For example, conductive carbon included in the inks may include one or more of graphene, graphite, carbon nano-onions, carbon black, carbon fibers, carbon nanofibers, amorphous carbon, activated carbon, charcoal, carbon buckyballs, carbon nanobuds, and pyrolytic carbon, among other forms of conductive carbon.

Printable inks for printing a separator can comprise one or more thermally conductive additives, e.g., graphene oxide. As described herein, graphite is a three-dimensional carbon based material made up of millions of layers of graphene, as understood in the relevant industry. Graphite oxide refers to a material formed by oxidation of graphite using strong oxidizing agents, thereby introducing oxygenated functionalities to graphite. For example, graphite oxide may expand the layer separation, or make the material hydrophilic. Graphite oxide can be exfoliated, e.g., in water using sonication, thereby producing a two-dimensional material comprising a single or a few layers of graphite oxide, which is referred to in the industry and herein a graphene oxide (GO). According to various embodiments described herein, GO refers to a structure having one or more layers but fewer than about 100, 50, 20, 10 or 5 sheets, any number of sheets within a range defined by any of these values.

According to various embodiments, GO can have a carbon-to-oxide ratio between about 1 to 100, 1 to 2, 2 to 5, 5 to 10, 10 to 15, 15 to 20, 20 to 25, 25 to 30, 30 to 35, 35 to 40, 40 to 45, 45 to 50, 50 to 55, 55 to 60, 60 to 65, 65 to 70, 70 to 75, 75 to 80, 80 to 85, 85 to 90, 90 to 95, 95 to 100, or a ratio within a range defined by any of these values. For instance, according to some embodiments, GO sheets have a mean carbon-to-oxygen ratio of about 2:1 to about 20:1 or about 5:1 to about 20:1.

Other embodiments of thermally conductive additives are possible. For example, the conductive additives can include one or more of boron nitride, beryllium oxide and other thermally conductive dielectric materials.

Various materials included in the inks for forming the layers of the supercapacitor, including coated diatoms, CNTs, conductive carbons, thermally conductive additives can have particle size ranging from 1 nm to 100 microns.

Printable inks for printing one or more layers of a supercapacitor, e.g., an electrode and/or a separator layers, can include a binder. The binder can include any component and composition of binders in the inks and electrodes as described herein. Examples of binders that can be used include styrene butadiene rubber (SBR), polyvinyl pyrrolidone (PVP), polyvinylidene fluoride, polyvynylidene fluoride-trifluoroethylene, polytetrafluoroethylene, polydimethylsiloxane, polyethelene, polypropylene, polyethylene oxide, polypropylene oxide, polyethylene glycolhexafluoropropylene, polyethylene terefphtalatpolyacrylonitryle, polyvinyl butyral, polyvinylcaprolactam, polyvinyl chloride; polyimide polymers and copolymers (including aliphatic, aromatic and semi-aromatic polyimides), polyamides, polyacrylamide, acrylate and (meth)acrylate polymers and copolymers such as polymethylmethacrylate, polyacrylonitrile,

acrylonitrile butadiene styrene, allylmethacrylate, polystyrene, polybutadiene, polybutylene terephthalate, polycarbonate, polychloroprene, polyethersulfone, nylon, styrene-acrylonitrile resin; polyethylene glycols, clays such as hectorite clays, garamite clays, organomodified clays; saccharides and polysaccharides such as guar gum, xanthan gum, starch, butyl rubber, agarose, pectin; celluloses and modified celluloses such as hydroxyl methylcellulose, methylcellulose, ethyl cellulose, propyl methylcellulose, methoxy cellulose, methoxy methylcellulose, methoxy propyl methylcellulose, hydroxy propyl methylcellulose, carboxy methylcellulose, hydroxy ethylcellulose, ethyl hydroxyl ethylcellulose, cellulose ether, cellulose ethyl ether, chitosan as well as their polymeric precursors or polymerizable precursors.

Printable inks for printing one or more layers of a supercapacitor, e.g., electrode and/or separator layers, can include a gelling polymer. The gelling polymer can include any component and composition of gelling polymers in the inks and electrodes as described herein. Examples of gelling polymers that can be used include polyvinylidene fluoride, polyacrylic acid, polyethylene oxide, polyvinyl alcohol.

According to various embodiments, all polymers included in the inks have suitable chemical, thermal and electrochemical stability such that they can be formed into printed layers.

Electrolytes for Supercapacitors

The energy density (E) of supercapacitors can be expressed as

$$E=CV^2/2, \quad \text{Eq. 7}$$

where C is the capacitance and V is the voltage. The voltage to which supercapacitors can be charged depends on, among other things, the electrochemical potential window of the electrolyte. Because of the strong dependence of energy density on voltage (proportional to square root of voltage), the electrochemical potential windows of electrolytes can have a substantial impact on the energy density, sometimes a larger impact on the energy density than the capacitance.

Operating electrochemical potential windows of typical aqueous electrolytes is 1-1.3V (hydrogen/oxygen evolution occur if one exceeds this voltage). Organic based electrolytes can have potential windows of 2.5-2.7V. To obtain significantly higher potential windows, e.g., 3.5-4.5V or even higher, electrolytes according to some embodiments include ionic liquids.

According to various embodiments, the electrolytes included in the supercapacitors have wide electrochemical potential window (for higher energy density), have higher ionic conductivity (low resistance and higher power), have higher chemical stability to other components, have wide temperature operating range, have low volatility and flammability, are environmentally friendly and/or are lower in cost, among other possible advantages.

As described herein, an electrolyte includes an electrolyte salt (or acid, base) and a solvent. The solvent can be aqueous or organic. Advantageously, solvents can have relatively high boiling point (above 80° C.). The solvents according to embodiments also have relatively slow evaporation rate to reduce solvent loss during ink mixing and printing as well as influencing the ink shelf life. The slow evaporation rate also increases lifetime of the supercapacitor. The solvents may be selected to dissolve various polymers described above, or serve as a medium for forming polymer suspensions as part of inks. The solvents may be selected to improve rheology of the inks. The remnants of some solvents in dried layers can improve the electrical performance of the supercapacitor.

To achieve these and/or other advantages, solvents can include one or more of water and alcohols such as methanol, ethanol, N-propanol (including 1-propanol, 2-propanol (isopropanol or IPA), 1-methoxy-2-propanol), butanol (including 1-butanol, 2-butanol (isobutanol)), pentanol (including 1-pentanol, 2-pentanol, 3-pentanol), hexanol (including 1-hexanol, 2-hexanol, 3-hexanol), octanol, N-octanol (including 1-octanol, 2-octanol, 3-octanol), tetrahydrofurfuryl alcohol (THFA), cyclohexanol, cyclopentanol, terpineol; lactones such as butyl lactone; ethers such as methyl ethyl ether, diethyl ether, ethyl propyl ether, and polyethers; ketones, including diketones and cyclic ketones, such as cyclohexanone, cyclopentanone, cycloheptanone, cyclooctanone, acetone, benzophenone, acetylacetone, acetophenone, cyclopropanone, isophorone, methyl ethyl ketone; esters such ethyl acetate, dimethyl adipate, propylene glycol monomethyl ether acetate, dimethyl glutarate, dimethyl succinate, glycerin acetate, carboxylates; carbonates such as propylene carbonate; polyols (or liquid polyols), glycerols and other polymeric polyols or glycols such as glycerin, diol, triol, tetraol, pentanol, ethylene glycols, diethylene glycols, polyethylene glycols, propylene glycols, dipropylene glycols, glycol ethers, glycol ether acetates 1,4-butanediol, 1,2-butanediol, 2,3-butanediol, 1,3-propanediol, 1,4-butanediol, 1,5-pentanediol, 1,8-octanediol, 1,2-propanediol, 1,3-butanediol, 1,2-pentanediol, etohexadiol, p-menthane-3,8-diol, 2-methyl-2,4-pentanediol; tetramethyl urea, n-methylpyrrolidone, acetonitrile, tetrahydrofuran (THF), dimethyl formamide (DMF), N-methyl formamide (NMF), dimethyl sulfoxide (DMSO); thionyl chloride; sulfuryl chloride; dibasic ester, diethylene glycol monoethyl ether acetate, combinations thereof, and the like.

Organic solvents can include one or more of acetonitrile, propylene carbonate, ethylene carbonate, diethyl carbonate, dimethyl carbonate, ethyl acetate, 1,1,1,3,3,3-hexafluoropropan-2-ol, adiponitrile, 1,3-propylene sulfite, butylene carbonate, Y-Butyrolactone, Y-Valerolactone, propionitrile, glutaronitrile, adiponitrile, methoxyacetonitrile, 3-methoxypropionitrile, N,N-Dimethylformamide, N,N-Dimethylacetamide, N-Methylpyrrolidinone, N-Methyloxazolidinone, N,N"-Dimethylimidazolininone, nitromethane, nitroethane, sulfonate, 3-Methylsulfonate, dimethylsulfoxide, trimethyl phosphate, combinations thereof, and the like.

Electrolytes according to some embodiments include ionic liquids (ILs). As described herein, IL refers to a salt in the liquid state at operation temperatures of the supercapacitors. For example, without limitation, IL can be in the liquid molten form at temperature below 100° C. Some ILs can consist essentially of ions, including a cation and an anion. The ILs can include combinations of the following example cations and anions.

Examples of cations that can be included in the ILs for supercapacitors include butyltrimethylammonium, 1-ethyl-3-methylimidazolium, 1-butyl-3-methylimidazolium, 1-methyl-3-propylimidazolium, 1-hexyl-3-methylimidazolium, choline, ethylammonium, tributylmethylphosphonium, tributyl(tetradecyl)phosphonium, trihexyl(tetradecyl) phosphonium, 1-ethyl-2,3-methylimidazolium, 1-butyl-1-methylpiperidinium, diethylmethylsulfonium, 1-methyl-3-propylimidazolium, 1-ethyl-3-methylimidazolium, 1-methyl-1-propylpiperidinium, 1-butyl-2-methylpyridinium, 1-butyl-4-methylpyridinium, 1-butyl-1-methylpyrrolidinium, diethylmethylsulfonium, combinations thereof, and the like.

Examples of anions that can be included in the ILs for supercapacitors include tris(pentafluoroethyl)trifluorophosphate, trifluoromethanesulfonate, hexafluorophosphate, tetrafluoroborate, ethyl sulfate, dimethyl phosphate, methansulfonate, triflate, tricyanomethanide, dibutylphosphate, bis(trifluoromethylsulfonyl)imide, bis-2,4,4-(trimethylpentyl) phosphinate, iodide, chloride, bromide, nitrate, combinations thereof, and the like.

According to some embodiments, the electrolyte or the IL of the supercapacitors additionally includes one or more salts dissolved in the electrolyte or dissolved in the IL when present. Salts in the electrolytes include combinations of a cation and an anion.

The cation of the salt can be selected from one or more of zinc, sodium, potassium, magnesium, calcium, aluminum, lithium, barium, combinations thereof, and the like.

The anion of the salt can be selected from one or more of chloride, bromide, fluoride, bis(trifluoromethanesulfonyl) imide, sulfate, bisulfite, nitrate, nitrite, carbonate, hydroxide, perchloride, bicarbonate, tetrafluoroborate, methansulfonate, acetate, phosphate, citrate, hexafluorophosphate, combinations thereof, and the like.

The electrolyte can include an organic salt, an inorganic salt, an acid, or a base.

Examples of organic salts include tetraethylammonium tetrafluoroborate, tetraethylammonium difluoro(oxalate)borate, methylammonium tetrafluoroborate, triethylmethylammonium tetrafluoroborate, tetrafluoroboric acid dimethyldi ethylammonium, triethylmethylammonium tetrafluoroborate, tetrapropylammonium tetrafluoroborate, methyltributylammonium tetrafluoroborate, tetrabutylammonium tetrafluoroborate, tetrahexylammonium tetrafluoroborate, tetramethylammonium tetrafluoroborate, tetraethyl phosphonium tetrafluoroborate, tetrapropylphosphonium tetrafluoroborate, tetrabutylphosphonium, tetrafluoroborate, combinations thereof, and the like.

Examples of acid include H_2SO_4, HCl, HNO_3, $HClO_4$, combinations thereof, and the like.

Examples of base include KOH, NaOH, LiOH, NH_4OH, combinations thereof, and the like.

Examples of inorganic salts include LiCl, Li_2SO_4, $LiClO_4$, NaCl, Na_2SO_4, $NaNO_3$, KCl, K_2SO_4, KNO_3, $Ca(NO_3)_2$, $MgSO_4$, combinations thereof, and the like.

Any other salts, electrolytes or ionic liquids disclosed herein are possible.

Ionic liquids can serve as the electrolyte and/or be included as part of the electrolyte, with or without salts. Ionic liquids can be used with non-aqueous electrolytes and/or with water.

According to various embodiments, particular electrolytes can be selected to form gel electrolytes by mixing with polymers or other matrices.

Supercapacitor Configurations

The geometric arrangement of electrodes and the separator of supercapacitors according to various embodiments can have any one of the configurations illustrated on FIG. **7**. In some embodiments, the electrodes of the supercapacitor can be arranged symmetrically or asymmetrically. As described herein, when electrodes having opposing polarities (e.g., cathode and an anode or a positive electrode and a negative electrode) are configured symmetrically, both types of electrodes are configured to store charge predominantly as EDLCs or predominantly as pseudo capacitors.

As described herein, an electrode that is configured to store charge predominantly through one of the two types of storage mechanisms exhibits a capacitance value that arises predominantly from the type of storage mechanisms over the other. For example, when an electrode is configured to store energy predominantly through one of the electric double layer capacitance or pseudo capacitance mechanisms, at least 80%, 90%, 95%, 99%, or a value in a range defined by any of these values, of the net capacitance value may arise from the one of the electric double layer capacitance or pseudo capacitance mechanisms. For example, when the surface active material comprises one but not the other of (1) CNT or (2) manganese oxide and/or zinc oxide, the electrode may be predominantly configured as one but not the other of an EDLC or a pseudo capacitor. And when the surface active material comprises both (1) CNT and (2) manganese oxide and/or zinc oxide, the electrode may be predominantly configured as an EDLC when the relative amount of manganese oxide and/or zinc oxide is low compared to the relative amount of CNT, and vice versa.

When an electrode is configured to store energy substantially through both of the electric double layer capacitance and pseudo capacitance mechanisms, 20-80%, 30-70%, 40-60%, or a value in a range defined by any of these values, of the net capacitance value may arise from the one of the electric double layer capacitance or pseudo capacitance mechanisms, while the balance may substantially be attributable to the other of the electric double layer capacitance or pseudo capacitance mechanisms. For example, when the surface active material comprises both (1) CNT and (2) manganese oxide and/or zinc oxide, the electrode may be substantially configured as an EDLC as well as a pseudo capacitor when the relative amounts of both (1) CNT and (2) manganese oxide and/or zinc oxide are substantial or effective to give rise to the above percentage values of capacitance values attributable to each of the mechanisms.

When electrodes having opposing types polarities (e.g., cathode and an anode or a positive electrode and a negative electrode) are configured asymmetrically, one of the two types of electrodes is configured to store charge predominantly as one of a an EDLC or a pseudo capacitor, while the other one of the two types of electrodes is configured to store charge predominantly as the other of the EDLC or a pseudo capacitor.

When the electrodes of opposite charge types are configured symmetrically, the electrodes of both types of charge may include frustules having nanostructures of the same type. For example, electrodes of both types may include zinc-oxide, e.g., frustules having formed thereon zinc oxide (Zn_xO_y, e.g., ZnO) nanostructures, manganese-oxide, e.g., frustules having formed thereon manganese oxide (MnO_xO_y) nanostructures, and/or carbon, e.g., frustules having formed thereon carbon nanostructures, e.g., carbon nanotube (CNTs). When the electrodes of opposite charge types are configured asymmetrically, the electrodes of different types of charge may include frustules having different ones of these nanostructures. Symmetric supercapacitors having electrodes of both charge types that include the same metal oxide on frustules, e.g., Zn_xO_y or Mn_xO_y are predominantly pseudo capacitors. Symmetric supercapacitors having electrodes of both charge types that include carbon nanostructures on frustules, e.g., CNT, are predominantly EDLCs. Asymmetric supercapacitors having an electrode of first charge type that includes one of transition metal oxides and an electrode of second charge type that includes CNT on frustules without transition metal oxides, e.g., first and second surface active materials that include Mn_xO_y and CNT, respectively, and Zn_xO_y and CNT, respectively, are hybrid capacitors that combine characteristics of both a pseudo capacitor on one electrode and an EDLC on the other electrode.

Supercapacitors can comprise a suitable commercially available separator or a printed separator, e.g., a printed separator comprising frustules and/or graphene oxide.

In some embodiments, supercapacitors comprise an ionic liquid that serves as an electrolyte. In some embodiments, supercapacitors comprise a combination of an ionic liquid and one of both of a salt and a solvent serving as an electrolyte. In some embodiments, the electrolyte essentially consists of an ionic liquid.

A current collector can comprise a suitable electrically conducting material, e.g. Al, Cu, Ni, stainless steel, graphite/graphene/CNTs, foil, etc. The foils can be laminated with a polymer from one side. A current collector can be formed from a printed conductive ink. The ink can include Al, Ni, Ag, Cu, Bi, carbon, carbon nanotubes, graphene, graphite and other conductive metals and mixture of thereof.

Substrates on which different layers are printed can be conductive or non-conductive. Advantageously, the various layers of the supercapacitors disclosed herein can be printed on flexible substrates having flexibility comparable to, e.g., a cloth. The substrates can include graphite paper, graphene paper, polyester film, polyimide film, Al foil, Cu foil, stainless foil, carbon foam, polycarbonate film, paper, coated paper, plastic coated paper, fiber paper and/or cardboard, to name a few.

After printing the various layers, supercapacitors can be encapsulated by lamination, e.g., by printing/depositing a protective layer, for example.

The supercapacitors can be printed in any suitable shape. Supercapacitors can be printed such that they are electrically connected in in parallel and/or electrically connected in series. Supercapacitors can be printed such that they are electrically connected in parallel and/or series with printed batteries.

Advantageously, the overall thickness of supercapacitor can be made extremely thin. The entire supercapacitor, including the substrate, can have a thickness of 10-50 microns, 50-100 microns, 100-200 microns, 200-300 microns, 300-400 microns, 400-500 microns, 500-600 microns, 600-700 microns, 700-800 microns 800-900 microns, 900-1000 microns, 1000-1200 microns, 1200-1400 microns, 1400-1600 microns, 1600-1800 microns, 1800-2000 microns, or a thickness in a range defined by any of these values.

Supercapacitor Fabrication Method

Advantageously, using the inks described above, one or more or all layers of the supercapacitor can be printed. The one or more layers or the entire supercapacitor can be printed using any of the printing techniques described herein. Example printing processes that can be used to print the one or more layers include coating, rolling, spraying, layering, spin coating, lamination and/or affixing processes, for example, screen printing, inkjet printing, electro-optical printing, electroink printing, photoresist and other resist printing, thermal printing, laser jet printing, magnetic printing, pad printing, flexographic printing, hybrid offset lithography, gravure and other intaglio printing, die slot deposition, among other suitable printing techniques.

The inks for printing one or more layers of the supercapacitor can be prepared by mixing various ink components described above, using any of the ink mixing techniques described herein, including mixing with a stir bar, mixing with a magnetic stirrer, vortexing (using a vortex machine), shaking (using a shaker), planetary centrifugal mixing, by rotation, three roll milling, ball milling, sonication and mixing using mortar and pestle, to name a few.

One or more layers printed using inks described above, including the electrodes and/or the separator, can be treated using various processes described above, including drying/curing techniques including short wave infrared (IR) radiation, medium wave IR-radiation, hot air conventional ovens, electron beam curing and near infrared radiation, among other techniques. When cured using convectional and IR ovens, the layers are subjected to a temperature range of 50-200° C., 75-175° C., 100-150° C. or any temperature in a range defined by any of these values, for a duration of 1 to 60 minutes, 2 to 40 minutes, 3-15 minutes, or any duration in a range defined by any of these values.

The one or more layers printed using inks described above, including the electrodes and/or the separators, can be cured/dried using near-infrared (NIR) light energy, using a suitable equipment configured to generate such light source. One example equipment that can be used is available from Adphos Group. Using NIR light energy to dry/cure the printed layers can advantageously include shorter drying times, e.g., by as much as an order of magnitude shorter (e.g., in seconds rather than minutes) than drying times employed using IR or conventional ovens. The inventors have discovered that the NIR radiation penetrates deeper into the printed layers printed more effectively and quickly, thereby removing solvents from the entire thickness of the printed layers more effectively and quickly. To facilitate even faster drying of the printed layers, when NIR radiation is used, heat-absorbing particles can be included in the ink for the printed layers, thereby further improving the efficiency of the drying process. In some printed layers, such as electrodes, surface active materials such as CNTs, Mn_xO_y or Zn_xO_y as well as other electrically conductive carbon included in the printed electrode layers can serve as heat-absorbing particles to facilitate drying of the printed layers. In some printed layers, such as separators, thermally conductive additives, graphene oxide (GO), may be added to serve as heat-absorbing particles to facilitate drying of the printed layers. As described herein, because the thermally conductive additive such as GO can be a good electrical insulator, the separator advantageously maintains the electrically insulating characteristics, while serving as a heat absorbing material. The inventors have found, when included as part of a printed layer such as a printed separator layer, GO may reduce the drying time by as much as one order of magnitude, e.g., from tens or minutes to tens of seconds. When NIR radiation is used, the layers can be dried/cured for a duration of 1-60 sec., 1-45 sec., 1-30 sec. or for a duration in a range defined by any of these values, which is significantly shorter than drying/curing times that maybe employed using other light sources, e.g., IR light sources.

Experimental Performance of Supercapacitors

FIGS. **16**A and **16**B illustrate experimental measurements performed on a supercapacitor having symmetric printed electrodes, where each of the electrodes having opposite polarities comprises frustules having formed thereon zinc oxide (Zn_xO_y, e.g., ZnO) nanostructures, such that the supercapacitor is configured as a pseudo capacitor. FIG. **16**A illustrates a charge/discharge curve measured on a supercapacitor having square electrodes (1.6 cm×1.6 cm). The capacitor was charged/discharged at 1 mA, and the charge time was 500 sec. The measured capacitance was about 0.06 F. The cut-off voltage for calculations was 1V. FIG. **16**B illustrates a charge/discharge curve measured on a similar capacitor as that illustrated in FIG. **16**A, in which the supercapacitor was charged/discharged at a higher current

10 mA. The cut-off voltage for charging was 3V. The measured capacitance was about 0.04 F. The cut-off voltage for calculations was 1V.

FIGS. **17**A-**17**D illustrate experimental measurements performed on a supercapacitor having symmetric printed electrodes, where each of the electrodes having opposite polarities comprises frustules having formed thereon manganese oxide (Mn_xO_y) nanostructures, such that the supercapacitor is configured as a pseudo capacitor. FIG. **17**A illustrates a charge/discharge curve measured on a supercapacitor having square electrodes (1.6 cm×1.6 cm). The capacitor was charged/discharged at 2 mA, and the charge time was 500 sec. The measured capacitance was about 0.14 F. The cut-off voltage for calculations was 1V.

FIG. **17**B illustrates a charge/discharge curve measured on a supercapacitor having square electrodes (1.6 cm×1.6 cm). The capacitor was charged at 40 mA for 3 sec. and discharged at 0.4 mA. The measured average capacitance was about 0.06 F. The cut-off voltage for calculations was 1V. The capacitance value was observed to increase with cycling. While only a few cycles are shown, the capacitor was successfully cycled 1000 times without degradation. As illustrated, the capacitors were demonstrated to charge relatively quickly, which is an advantageous property of supercapacitors over batteries, as described above.

FIG. **17**C illustrates a discharge curve measured on a supercapacitor having square electrodes (1.6 cm×1.6 cm). The capacitor was charged at 40 mA for 3 sec. and discharged at 0.4 mA. The measured average capacitance was about 0.055 F. The cut-off voltage for calculations was 1V. While only one cycle (330th cycle) is shown for illustrative purposes, the capacitor was successfully cycled more than 1000 times without substantial deterioration.

FIG. **17**D illustrates a discharge curve measured on a supercapacitor having square electrodes (1.6 cm×1.6 cm). The capacitor was charged at 40 mA for 3 sec. and discharged at 0.4 mA. The measured average capacitance was about 0.061 F. The cut-off voltage for calculations was 1V. While only one cycle (1000th cycle) is shown for illustrative purposes, the capacitor was successfully cycled more than 1000 times without substantial deterioration.

FIGS. **18**A-**18**E illustrate experimental measurements performed on a supercapacitor having asymmetric printed electrodes, where one of the electrodes having opposite polarities comprises frustules having formed thereon manganese oxide (Mn_xO_y) nanostructures, while the other of the electrodes comprises frustules having formed thereon CNT, such that the supercapacitor is configured as a hybrid supercapacitor. The specific capacitance (C_{sp}), which can be defined as the measured capacitance multiplied by the specific surface area, of 100-340 F/g at specific current of 0.01-1 A/g was obtained based on the amount of surface active material.

FIG. **18**A illustrates a discharge curve measured on a supercapacitor having square electrodes (2.54. cm×2.54 cm). The capacitor was charged at a constant voltage of 2V for 30 minutes and discharged at 2 mA. The measured capacitance was about 2.21 F. The cut-off voltage for calculations was 1V.

FIG. **18**B illustrates a discharge curve measured on a supercapacitor having square electrodes (2.54. cm×2.54 cm). The capacitor was charged at a constant voltage of 2V for 30 minutes and discharged at 2 mA. The measured capacitance was about 3.26 F. The cut-off voltage for calculations was 1V.

FIG. **18**C illustrates a discharge curve measured on a supercapacitor having square electrodes (2.54. cm×2.54 cm). The capacitor was charged at constant voltage of 3V for 30 minutes and discharged at 2 mA. The measured capacitance was about 3.86 F. The cut-off voltage for calculations was 1V.

FIG. **18**D illustrates a charge/discharge curve measured on a supercapacitor having square electrodes (2.54. cm×2.54 cm). The capacitor was charged at 0.1 A for 2 sec. and discharged at 1 mA. The measured capacitance was about 1.36 F. The cut-off voltage for calculations was 1V. As illustrated, the capacitor charged relatively quickly, which is an advantageous property of supercapacitors over batteries, as described above.

FIG. **18**E illustrates a charge/discharge curve measured on a supercapacitor having square electrodes (2.54. cm×2.54 cm). The capacitor was charged to 4.5V at 2 mA for 2 sec. and discharged at 1 mA. The cut-off voltage for calculations was 2V. As illustrated, the capacitors charged relatively quickly, which is an advantageous property of supercapacitors over batteries, as described above.

FIGS. **19**A-**19**B illustrate experimental measurements performed on a supercapacitor having symmetric printed electrodes, where each of the electrodes having opposite polarities comprises frustules having formed thereon CNT, such that the supercapacitor is configured as a double layer supercapacitor. The specific capacitance (C_{sp}) was 50-100 F/g at specific current of 0.01-1 A/g based on the amount of surface active material.

FIG. **19**A illustrates a charge/discharge curve measured on a supercapacitor having square electrodes (1.6 cm×1.6 cm). The capacitor was charged at 1 mA for 500 sec. and discharged at 1 mA. The measured capacitance was about 0.08 F. The cut-off voltage for calculations was 1V.

FIG. **19**B illustrates a discharge curve measured on a supercapacitor having square electrodes (2.54. cm×2.54 cm). The capacitor was charged to 3V at 5 mA and discharged at 5 mA. The measured capacitance was about 0.06 F. The cut-off voltage for calculations was 1V.

EXAMPLE EMBODIMENTS

The following example embodiments identify some possible permutations of combinations of features disclosed herein, although other permutations of combinations of features are also possible.

1. A printed energy storage device comprising:
   a first electrode;
   a second electrode; and
   a separator between the first electrode and the second electrode, at least one of the first electrode, the second electrode, and the separator including frustules.

2. The device of Embodiment 1, wherein the separator includes the frustules.

3. The device of Embodiment 1 or 2, wherein the first electrode includes the frustules.

4. The device of any of Embodiments 1-3, wherein the second electrode includes the frustules.

5. The device of any one of Embodiments 1-4, wherein the frustules have a substantially uniform property.

6. The device of Embodiment 5, wherein property comprises shape.

7. The device of Embodiment 6, wherein the shape comprises a cylinder, a sphere, a disc, or a prism.

8. The device of any of Embodiments 5-7, wherein the property comprises a dimension.

9. The device of Embodiment 8, wherein the dimension comprises diameter.

10. The device of Embodiment 9, wherein the diameter is in a range from about 2 μm to about 10 μm.

11. The device of Embodiment 8, wherein the dimension comprises length.

12. The device of Embodiment 9, wherein the length is in a range from about 5 μm to about 20 μm.

13. The device of Embodiment 8, wherein the dimension comprises a longest axis.

14. The device of Embodiment 9, wherein the longest axis is in a range from about 5 μm to about 20 μm.

15. The device of any of Embodiments 5-14, wherein the property comprises porosity.

16. The device of Embodiment 15, wherein the porosity is in a range from about 20% to about 50%.

17. The device of any of Embodiments 5-16, wherein the property comprises mechanical strength.

18. The device of any of Embodiment 1-17, wherein the frustules comprise a surface modifying structure.

19. The device of Embodiment 18, wherein the surface modifying structure includes a conductive material.

20. The device of Embodiment 19, wherein the conductive material includes at least one of silver, aluminum, tantalum, copper, lithium, magnesium, and brass.

21. The device of any of Embodiments 18-20, wherein the surface modifying structure includes zinc oxide (ZnO).

22. The device of any of Embodiments 18-21, wherein the surface modifying structure includes a semiconductor.

23. The device of Embodiment 22, wherein the semiconductor includes at least one of silicon, germanium, silicon germanium, and gallium arsenide.

24. The device of any of Embodiments 18-23, wherein the surface modifying structure comprises at least one of a nanowire, a nanoparticle, and a structure having a rosette shape.

25. The device of any of Embodiments 18-24, wherein the surface modifying structure is on an exterior surface of the frustules.

26. The device of any of Embodiments 18-25, wherein the surface modifying structure is on an interior surface of the frustules.

27. The device of any of Embodiments 1-26, wherein the frustules comprise a surface modifying material.

28. The device of Embodiment 27, wherein the surface modifying material includes a conductive material.

29. The device of Embodiment 28, wherein the conductive material includes at least one of silver, aluminum, tantalum, copper, lithium, magnesium, and brass.

30. The device of any of Embodiments 27-29, wherein the surface modifying material includes zinc oxide (ZnO).

31. The device of any of Embodiments 27-30, wherein the surface modifying material includes a semiconductor.

32. The device of Embodiment 31, wherein the semiconductor includes at least one of silicon, germanium, silicon germanium, and gallium arsenide.

33. The device of any of Embodiments 27-32, wherein the surface modifying material is on an exterior surface of the frustules.

34. The device of any of Embodiments 37-33, wherein the surface modifying material is on an interior surface of the frustules.

35. The device of any of Embodiments 1-34, wherein the first electrode comprises a conductive filler.

36. The device of any of Embodiments 1-35, wherein the second electrode comprises a conductive filler.

37. The device of Embodiment 34 or 35, wherein the conductive filler comprises graphitic carbon.

38. The device of any of Embodiments 35-37, wherein the conductive filler comprises graphene.

39. The device of any of Embodiments 1-38, wherein the first electrode comprises an adherence material.

40. The device of any of Embodiments 1-39, wherein the second electrode comprises an adherence material.

41. The device of any of Embodiments 1-40, wherein the separator comprises an adherence material.

42. The device of any of Embodiments 39-41, wherein the adherence material comprises a polymer.

43. The device of any of Embodiments 1-42, wherein the separator comprises an electrolyte.

44. The device of Embodiment 43, wherein the electrolyte comprises at least one of an ionic liquid, an acid, a base, and a salt.

45. The device of Embodiment 43 or 44, wherein the electrolyte comprises an electrolytic gel.

46. The device of any of Embodiments 1-45, further comprising a first current collector in electrical communication with the first electrode.

47. The device of any of Embodiments 1-46, further comprising a second current collector in electrical communication with the second electrode.

48. The device of any of Embodiments 1-47, wherein the printed energy storage device comprises a capacitor.

49. The device of any of Embodiments 1-47, wherein the printed energy storage device comprises a supercapacitor.

50. The device of any of Embodiments 1-47, wherein the printed energy storage device comprises a battery.

51. A system comprising a plurality of the devices of any of Embodiments 1-50 stacked on top of each other.

52. An electrical device comprising the device of any of Embodiments 1-50 or the system of Embodiment 51.

53. A membrane for a printed energy storage device, the membrane comprising frustules.

54. The membrane of Embodiment 53, wherein the frustules have a substantially uniform property.

55. The membrane of Embodiment 54, wherein the property comprises shape.

56. The membrane of Embodiment 55, wherein the shape comprises a cylinder, a sphere, a disc, or a prism.

57. The membrane of any of Embodiments 54-56, wherein the property comprises a dimension.

58. The membrane of Embodiment 57, wherein the dimension comprises diameter.

59. The membrane of Embodiment 58, wherein the diameter is in a range from about 2 μm to about 10 μm.

60. The membrane of any of Embodiments 54-59, wherein the dimension comprises length.

61. The membrane of Embodiment 60, wherein the length is in a range of about 5 to about 20 μm.

62. The membrane of any of Embodiments 54-61, wherein the dimension comprises a longest axis.

63. The membrane of Embodiment 62, wherein the longest axis is in a range of about 5 μm to about 20 μm.

64. The membrane of any of Embodiments 54-63, wherein the property comprises porosity.

65. The membrane of Embodiment 64, wherein the porosity is in a range from about 20% to about 50%.

66. The membrane of any of Embodiments 54-65, wherein the property comprises mechanical strength.

67. The membrane of any of Embodiments 53-66, wherein the frustules comprise a surface modifying structure.

68. The membrane of Embodiment 67, wherein the surface modifying structure includes a conductive material.

69. The membrane of Embodiment 68, wherein the conductive material includes at least one of silver, aluminum, tantalum, copper, lithium, magnesium, and brass.

70. The membrane of any of Embodiments 67-69, wherein the surface modifying structure includes zinc oxide (ZnO).

71. The membrane of any of Embodiments 67-70, wherein the surface modifying structure includes a semiconductor.

72. The membrane of Embodiment 71, wherein the semiconductor includes at least one of silicon, germanium, silicon germanium, and gallium arsenide.

73. The membrane of any of Embodiments 67-72, wherein the surface modifying structure comprises at least one of a nanowire, a nanoparticle, and a structure having a rosette shape.

74. The membrane of any of Embodiments 67-73, wherein the surface modifying structure is on an exterior surface of the frustules.

75. The membrane of any of Embodiments 67-74, wherein the surface modifying structure is on an interior surface of the frustules.

76. The membrane of any of Embodiments 53-75, wherein the frustules comprises a surface modifying material.

77. The membrane of Embodiment 76, wherein surface modifying material includes a conductive material.

78. The membrane of Embodiment 77, wherein the conductive material includes at least one of silver, aluminum, tantalum, copper, lithium, magnesium, and brass.

79. The membrane of any of Embodiments 76-78, wherein the surface modifying material includes zinc oxide (ZnO).

80. The membrane of any of Embodiments 76-79, wherein the surface modifying material includes a semiconductor.

81. The membrane of Embodiment 80, wherein the semiconductor includes at least one of silicon, germanium, silicon germanium, and gallium arsenide.

82. The membrane of any of Embodiments 76-81, wherein the surface modifying material is on an exterior surface of the frustules.

83. The membrane of any of Embodiments 76-82, wherein the surface modifying material is on an interior surface of the frustules.

84. The membrane of any of Embodiments 83-83, further comprising a conductive filler.

85. The membrane of Embodiment 84, wherein the conductive filler comprises graphitic carbon.

86. The membrane of Embodiment 84 or 85, wherein the conductive filler comprises graphene.

87. The membrane of any of Embodiments 53-86, further comprising an adherence material.

88. The membrane of Embodiment 87, wherein the adherence material comprises a polymer.

89. The membrane of any of Embodiments 53-88, further comprising an electrolyte.

90. The membrane of Embodiment 89, wherein the electrolyte comprises at least one of an ionic liquid, an acid, a base, and a salt.

91. The membrane of Embodiment 89 or 90, wherein the electrolyte comprises an electrolytic gel.

92. An energy storage device comprising the membrane of any of Embodiments 53-91.

93. The device of Embodiment 92, wherein the printed energy storage device comprises a capacitor.

94. The device of Embodiment 92, wherein the printed energy storage device comprises a supercapacitor.

95. The device of Embodiment 92, wherein the printed energy storage device comprises a battery.

96. A system comprising a plurality of the devices of any of Embodiments 92-95 stacked on top of each other.

97. An electrical device comprising the device of any of Embodiments 92-95 or the system of Embodiment 96.

98. A method of manufacturing a printed energy storage device, the method comprising:

forming a first electrode;

forming a second electrode; and

forming a separator between the first electrode and the second electrode, at least one of the first electrode, the second electrode, and the separator including frustules.

99. The method of Embodiment 98, wherein the separator includes the frustules.

100. The method of Embodiment 99, wherein forming the separator includes forming a dispersion including the frustules.

101. The method of Embodiment 99 or 100, wherein forming the separator includes screen printing the separator.

102. The method of Embodiment 99, wherein forming the separator includes forming a membrane including the frustules.

103. The method of Embodiment 102, wherein forming the separator includes roll-to-roll printing the membrane including the separator.

104. The method of any of Embodiments 98-103, wherein the first electrode includes the frustules.

105. The method of Embodiment 104, wherein forming the first electrode includes forming a dispersion including the frustules.

106. The method of Embodiment 104 or 105, wherein forming the first electrode includes screen printing the first electrode.

107. The method of Embodiment 104, wherein forming the first electrode includes forming a membrane including the frustules.

108. The method of Embodiment 107, wherein forming the first electrode includes roll-to-roll printing the membrane including the first electrode.

109. The method of any of Embodiments 98-108, wherein the second electrode includes the frustules.

110. The method of Embodiment 109, wherein forming the second electrode includes forming a dispersion including the frustules.

111. The method of Embodiment 109 or 110, wherein forming the second electrode includes screen printing the second electrode.

112. The method of Embodiment 109, wherein forming the second electrode includes forming a membrane including the frustules.

113. The method of Embodiment 112, wherein forming the second electrode includes roll-to-roll printing the membrane including the second electrode.

114. The method of any of Embodiments 98-113, further comprising sorting the frustules according to a property.

115. The method of Embodiment 114, wherein the property comprises at least one of shape, dimension, material, and porosity.

116. An ink comprising:

a solution; and

frustules dispersed in the solution.

117. The ink of Embodiment 116, wherein the frustules have a substantially uniform property.

118. The ink of Embodiment 117, wherein the property comprises shape.

119. The ink of Embodiment 118, wherein the shape comprises a cylinder, a sphere, a disc, or a prism.

120. The ink of any of Embodiments 117-119, wherein the property comprises a dimension.

121. The ink of Embodiment 120, wherein the dimension comprises diameter.

122. The ink of Embodiment 121, wherein the diameter is in a range from about 2 μm to about 10 μm.

123. The ink of any of Embodiments 117-122, wherein the dimension comprises length.

124. The ink of Embodiment 123, wherein the length is in a range of about 5 μm to about 20 μm.

125. The ink of any of Embodiments 117-124, wherein the dimension comprises a longest axis.

126. The ink of Embodiment 125, wherein the longest axis is in a range of about 5 to about 20 μm.

127. The ink of any of Embodiments 117-126, wherein the property comprises porosity.

128. The ink of Embodiment 127, wherein the porosity is in a range from about 20% to about 50%.

129. The ink of any of Embodiments 117-128, wherein the property comprises mechanical strength.

130. The ink of any of Embodiments 116-129, wherein the frustules comprise a surface modifying structure.

131. The ink of Embodiment 130, wherein the surface modifying structure includes a conductive material.

132. The ink of Embodiment 131, wherein the conductive material includes at least one of silver, aluminum, tantalum, copper, lithium, magnesium, and brass.

133. The ink of any of Embodiments 130-132, wherein the surface modifying structure includes zinc oxide (ZnO).

134. The ink of any of Embodiments 130-133, wherein the surface modifying structure includes a semiconductor.

135. The ink of Embodiment 134, wherein the semiconductor includes at least one of silicon, germanium, silicon germanium, and gallium arsenide.

136. The ink of any of Embodiments 130-135, wherein the surface modifying structure comprises at least one of a nanowire, a nanoparticle, and a structure having a rosette shape.

137. The ink of any of Embodiments 130-136, wherein the surface modifying structure is on an exterior surface of the frustules.

138. The ink of any of Embodiments 130-137, wherein the surface modifying structure is on an interior surface of the frustules.

139. The ink of any of Embodiments 116-138, wherein the frustules comprises a surface modifying material.

140. The ink of Embodiment 139, wherein surface modifying material includes a conductive material.

141. The ink of Embodiment 140, wherein the conductive material includes at least one of silver, aluminum, tantalum, copper, lithium, magnesium, and brass.

142. The ink of any of Embodiments 139-141, wherein the surface modifying material includes zinc oxide (ZnO).

143. The ink of any of Embodiments 139-142, wherein the surface modifying material includes a semiconductor.

144. The ink of Embodiment 143, wherein the semiconductor includes at least one of silicon, germanium, silicon germanium, and gallium arsenide.

145. The ink of any of Embodiments 139-144, wherein the surface modifying material is on an exterior surface of the frustules.

146. The ink of any of Embodiments 139-145, wherein the surface modifying material is on an interior surface of the frustules.

147. The ink of any of Embodiments 116-146, further comprising a conductive filler.

148. The ink of Embodiment 147, wherein the conductive filler comprises graphitic carbon.

149. The ink of Embodiment 147 or 148, wherein the conductive filler comprises graphene.

150. The ink of any of Embodiments 116-149, further comprising an adherence material.

151. The ink of Embodiment 150, wherein the adherence material comprises a polymer.

152. The ink of any of Embodiments 116-151, further comprising an electrolyte.

153. The ink of Embodiment 152, wherein the electrolyte comprises at least one of an ionic liquid, an acid, a base, and a salt.

154. The ink of Embodiment 152 or 153, wherein the electrolyte comprises an electrolytic gel.

155. A device comprising the ink of any of Embodiments 116-154.

156. The device of Embodiment 155, wherein the device comprises a printed energy storage device.

157. The device of Embodiment 156, wherein the printed energy storage device comprises a capacitor.

158. The device of Embodiment 156, wherein the printed energy storage device comprises a supercapacitor.

159. The device of Embodiment 156, wherein the printed energy storage device comprises a battery.

160. A method of extracting a diatom frustule portion, the method comprising:

dispersing a plurality of diatom frustule portions in a dispersing solvent;

removing at least one of an organic contaminant and an inorganic contaminant;

dispersing the plurality of diatom frustule portions in a surfactant, the surfactant reducing an agglomeration of the plurality of diatom frustule portions; and

extracting a plurality of diatom frustule portions having at least one common characteristic using a disc stack centrifuge.

161. The method of embodiment 160, wherein the at least one common characteristic comprises at least one of a dimension, a shape, a material, and a degree of brokenness.

162. The method of embodiment 161, wherein the dimension comprises at least one of a length and a diameter.

163. The method of any one of embodiments 160 to 162, wherein a solid mixture comprises the plurality of diatom frustule portions.

164. The method of embodiment 163, further comprising reducing a particle dimension of the solid mixture.

165. The method of embodiment 164, wherein reducing the particle dimension of the solid mixture is before dispersing the plurality of diatom frustule portions in the dispersing solvent.

166. The method of embodiment 164 or 165, wherein reducing the particle dimension comprises grinding the solid mixture.

167. The method of embodiment 166, wherein grinding the solid mixture comprises applying to the solid mixture at least one of a mortar and a pestle, a jar mill, and a rock crusher.

168. The method of any one of embodiments 163 to 167, further comprising extracting a component of the solid mixture having a longest component dimension that is

greater than a longest frustule portion dimension of the plurality of diatom frustule portions.

169. The method of embodiment 168, wherein extracting the component of the solid mixture comprises sieving the solid mixture.

170. The method of embodiment 169, wherein sieving the solid mixture comprises processing the solid mixture with a sieve having a mesh size from about 15 microns to about 25 microns.

171. The method of embodiment 169, wherein sieving the solid mixture comprises processing the solid mixture with a sieve having a mesh size from about 10 microns to about 25 microns.

172. The method of any one of embodiments 160 to 171, further comprising sorting the plurality of diatom frustule portions to separate a first diatom frustule portion from a second diatom frustule portion, the first diatom frustule portion having a greater longest dimension.

173. The method of embodiment 172, wherein the first diatom frustule portion comprises a plurality of unbroken diatom frustule portions.

174. The method of embodiment 172 or 173, wherein the second diatom frustule portion comprises a plurality of broken diatom frustule portions.

175. The method of any one of embodiments 172 to 174, wherein sorting comprises filtering the plurality of diatom frustule portions.

176. The method of embodiment 175, wherein filtering comprises disturbing agglomeration of the plurality of diatom frustule portions.

177. The method of embodiment 176, wherein disturbing agglomeration of the plurality of diatom frustule portions comprises stirring.

178. The method of embodiment 176 or 177, wherein disturbing agglomeration of the plurality of diatom frustule portions comprises shaking.

179. The method of any one of embodiments 176 to 178, wherein disturbing agglomeration of the plurality of diatom frustule portions comprises bubbling.

180. The method of any one of embodiments 175 to 179, wherein filtering comprises applying a sieve to the plurality of diatom frustule portions.

181. The method of embodiment 180, wherein the sieve has a mesh size from about 5 microns to about 10 microns.

182. The method of embodiment 180, wherein the sieve has a mesh size of about 7 microns.

183. The method of any one of embodiments 160 to 182, further comprising obtaining a washed diatom frustule portion.

184. The method of embodiment 183, wherein obtaining the washed diatom frustule portion comprises washing the plurality of diatom frustule portions with a cleaning solvent after removing the at least one of the organic contaminant and the inorganic contaminant.

185. The method of embodiment 183 or 184, wherein obtaining the washed diatom frustule portion comprises washing the diatom frustule portion having the at least one common characteristic with a cleaning solvent.

186. The method of embodiment 184 or 185, further comprising removing the cleaning solvent.

187. The method of embodiment 186, wherein removing the cleaning solvent comprises sedimenting the plurality of diatom frustule portions after removing at least one of the organic contaminant and the inorganic contaminant.

188. The method of embodiment 186 or 187, wherein removing the cleaning solvent comprises sedimenting the plurality of diatom frustule portions having the at least one common characteristic.

189. The method of embodiment 187 or 188, wherein sedimenting comprises centrifuging.

190. The method of embodiment 189, wherein centrifuging comprises applying a centrifuge suitable for large scale processing.

191. The method of embodiment 190, wherein centrifuging comprises applying at least one of a disc stack centrifuge, a decanter centrifuge, and a tubular bowl centrifuge.

192. The method of any one of embodiments 184 to 191, wherein at least one of the dispersing solvent and the cleaning solvent comprises water.

193. The method of any one of embodiments 160 to 192, wherein at least one of dispersing the plurality of diatom frustule portions in the dispersing solvent and dispersing the plurality of diatom frustule portions in the surfactant comprises sonicating the plurality of diatom frustules.

194. The method of any one of embodiments 160 to 193, wherein the surfactant comprises a cationic surfactant.

195. The method of embodiment 194, wherein the cationic surfactant comprises at least one of a benzalkonium chloride, a cetrimonium bromide, a lauryl methyl gluceth-10 hydroxypropyl dimonium chloride, a benzethonium chloride, a benzethonium chloride, a bronidox, a dmethyldioctadecylammonium chloride, and a tetramethylammonium hydroxide.

196. The method of any one of embodiments 160 to 195, wherein the surfactant comprises a non-ionic surfactant.

197. The method of embodiment 196, wherein the non-ionic surfactant comprises at least one of a cetyl alcohol, a stearyl alcohol, a cetostearyl alcohol, an oleyl alcohol, a polyoxyethylene glycol alkyl ether, an octaethylene glycol monododecyl ether, a glucoside alkyl ethers, a decyl glucoside, a polyoxyethylene glycol octylphenol ethers, an octylphenol ethoxylate (Triton X-100™), a nonoxynol-9, a glyceryl laurate, a polysorbate, and a poloxamer.

198. The method of any one of embodiments 160 to 197, further comprising dispersing the plurality of diatom frustules in an additive component.

199. The method of embodiment 198, wherein dispersing the plurality of diatom frustules in an additive component is before dispersing the plurality of diatom frustules in the surfactant.

200. The method of embodiment 198, wherein dispersing the plurality of diatom frustules in an additive component is after dispersing the plurality of diatom frustules in the surfactant.

201. The method of embodiment 198, wherein dispersing the plurality of diatom frustules in an additive component is at least partially simultaneous with dispersing the plurality of diatom frustules in the surfactant.

202. The method of any one of embodiments 198 to 201, wherein the additive component comprises at least one of a potassium chloride, an ammonium chloride, an ammonium hydroxide, and a sodium hydroxide.

203. The method of any one of embodiments 160 to 202, wherein dispersing the plurality of diatom frustule portions comprises obtaining a dispersion comprising about 1 weight percent to about 5 weight percent of the plurality of diatom frustule portions.

204. The method of any one of embodiments 160 to 203, wherein removing the organic contaminant comprises heating the plurality of diatom frustule portions in the presence of a bleach.

205. The method of embodiment 204, wherein the bleach comprises at least one of a hydrogen peroxide and a nitric acid.

206. The method of embodiment 205, wherein heating comprises heating the plurality of diatom frustule portions in a solution comprising an amount of hydrogen peroxide in a range from about 10 volume percent to about 20 volume percent.

207. The method of any one of embodiments 204 to 206, wherein heating comprises heating the plurality of diatom frustule portions for a duration of about 5 minutes to about 15 minutes.

208. The method of any one of embodiments 160 to 207, wherein removing the organic contaminant comprises annealing the plurality of diatom frustule portions.

209. The method of any one of embodiments 160 to 208, wherein removing the inorganic contaminant comprises combining the plurality of diatom frustule portions with at least one of a hydrochloric acid and a sulfuric acid.

210. The method of embodiment 209, wherein the combining comprises mixing the plurality of diatom frustule portions in a solution comprising about 15 volume percent to about 25 volume percent of hydrochloric acid.

211. The method of embodiment 210, wherein the mixing is for a duration of about 20 minutes to about 40 minutes.

212. A method of extracting a diatom frustule portion, the method comprising:

extracting a plurality of diatom frustule portions having at least one common characteristic using a disc stack centrifuge.

213. The method of embodiment 212, further comprising dispersing the plurality of diatom frustule portions in a dispersing solvent.

214. The method of embodiment 212 or 213, further comprising removing at least one of an organic contaminant and an inorganic contaminant.

215. The method of any one of embodiments 212 to 214, further comprising dispersing the plurality of diatom frustule portions in a surfactant, the surfactant reducing an agglomeration of the plurality of diatom frustule portions.

216. The method of any one of embodiments 212 to 215, wherein the at least one common characteristic comprises at least one of a dimension, a shape, a material, and a degree of brokenness.

217. The method of embodiment 216, wherein the dimension comprises at least one of a length and a diameter.

218. The method of any one of embodiments 212 to 217, wherein a solid mixture comprises the plurality of diatom frustule portions.

219. The method of embodiment 218, further comprising reducing a particle dimension of the solid mixture.

220. The method of embodiment 219, wherein reducing the particle dimension of the solid mixture is before dispersing the plurality of diatom frustule portions in the dispersing solvent.

221. The method of embodiment 219 or 220, wherein reducing the particle dimension comprises grinding the solid mixture.

222. The method of embodiment 221, wherein grinding the solid mixture comprises applying to the solid mixture at least one of a mortar and a pestle, a jar mill, and a rock crusher.

223. The method of any one of embodiments 219 to 222, further comprising extracting a component of the solid mixture having a longest component dimension that is greater than a longest frustule portion dimension of the plurality of diatom frustule portions.

224. The method of embodiment 223, wherein extracting the component of the solid mixture comprises sieving the solid mixture.

225. The method of embodiment 224, wherein sieving the solid mixture comprises processing the solid mixture with a sieve having a mesh size from about 15 microns to about 25 microns.

226. The method of embodiment 224, wherein sieving the solid mixture comprises processing the solid mixture with a sieve having a mesh size from about 10 microns to about 25 microns.

227. The method of any one of embodiments 212 to 226, further comprising sorting the plurality of diatom frustule portions to separate a first diatom frustule portion from a second diatom frustule portion, the first diatom frustule portion having a greater longest dimension.

228. The method of embodiment 227, wherein the first diatom frustule portion comprises a plurality of unbroken diatom frustule portions.

229. The method of embodiment 227 or 228, wherein the second diatom frustule portion comprises a plurality of broken diatom frustule portions.

230. The method of any one of embodiments 227 to 229, wherein sorting comprises filtering the plurality of diatom frustule portions.

231. The method of embodiment 230, wherein filtering comprises disturbing agglomeration of the plurality of diatom frustule portions.

232. The method of embodiment 231, wherein disturbing agglomeration of the plurality of diatom frustule portions comprises stirring.

233. The method of embodiment 231 or 282, wherein disturbing agglomeration of the plurality of diatom frustule portions comprises shaking.

234. The method of any one of embodiments 231 to 233, wherein disturbing agglomeration of the plurality of diatom frustule portions comprises bubbling.

235. The method of any one of embodiments 230 to 234, wherein filtering comprises applying a sieve to the plurality of diatom frustule portions.

236. The method of embodiment 235, wherein the sieve has a mesh size from about 5 microns to about 10 microns.

237. The method of embodiment 235, wherein the sieve has a mesh size of about 7 microns.

238. The method of any one of embodiments 212 to 237, further comprising obtaining a washed diatom frustule portion.

239. The method of embodiment 238, wherein obtaining the washed diatom frustule portion comprises washing the plurality of diatom frustule portions with a cleaning solvent after removing at least one of the organic contaminant and the inorganic contaminant.

240. The method of embodiment 238 or 239, wherein obtaining the washed diatom frustule portion comprises washing the diatom frustule portion having the at least one common characteristic with a cleaning solvent.

241. The method of embodiment 239 or 240, further comprising removing the cleaning solvent.

242. The method of embodiment 241, wherein removing the cleaning solvent comprises sedimenting the plurality of diatom frustule portions after removing the at least one of the organic contaminant and the inorganic contaminant.

243. The method of embodiment 241 or 242, wherein removing the cleaning solvent comprises sedimenting the plurality of diatom frustule portions having the at least one common characteristic.

244. The method of embodiment 242 or 243, wherein sedimenting comprises centrifuging.

245. The method of embodiment 244, wherein centrifuging comprises applying a centrifuge suitable for large scale processing.

246. The method of embodiment 245, wherein centrifuging comprises applying at least one of a disc stack centrifuge, a decanter centrifuge, and a tubular bowl centrifuge.

247. The method of any one of embodiments 240 to 246, wherein at least one of the dispersing solvent and the cleaning solvent comprises water.

248. The method of any one of embodiments 215 to 247, wherein at least one of dispersing the plurality of diatom frustule portions in the dispersing solvent and dispersing the plurality of diatom frustule portions in the surfactant comprises sonicating the plurality of diatom frustules.

249. The method of any one of embodiments 215 to 248, wherein the surfactant comprises a cationic surfactant.

250. The method of embodiment 249, wherein the cationic surfactant comprises at least one of a benzalkonium chloride, a cetrimonium bromide, a lauryl methyl gluceth-10 hydroxypropyl dimonium chloride, a benzethonium chloride, a benzethonium chloride, a bronidox, a dmethyldioctadecylammonium chloride, and a tetramethylammonium hydroxide.

251. The method of any one of embodiments 212 to 250, wherein the surfactant comprises a non-ionic surfactant.

252. The method of embodiment 251, wherein the non-ionic surfactant comprises at least one of a cetyl alcohol, a stearyl alcohol, a cetostearyl alcohol, an oleyl alcohol, a polyoxyethylene glycol alkyl ether, an octaethylene glycol monododecyl ether, a glucoside alkyl ethers, a decyl glucoside, a polyoxyethylene glycol octylphenol ethers, an octylphenol ethoxylate (Triton X-100™), a nonoxynol-9, a glyceryl laurate, a polysorbate, and a poloxamer.

253. The method of any one of embodiments 212 to 252, further comprising dispersing the plurality of diatom frustules in an additive component.

254. The method of embodiment 253, wherein dispersing the plurality of diatom frustules in an additive component is before dispersing the plurality of diatom frustules in the surfactant.

255. The method of embodiment 253, wherein dispersing the plurality of diatom frustules in an additive component is after dispersing the plurality of diatom frustules in the surfactant.

256. The method of embodiment 253, wherein dispersing the plurality of diatom frustules in an additive component is at least partially simultaneous with dispersing the plurality of diatom frustules in the surfactant.

257. The method of any one of embodiments 253 to 256, wherein the additive component comprises at least one of a potassium chloride, an ammonium chloride, an ammonium hydroxide, and a sodium hydroxide.

258. The method of any one of embodiments 213 to 257, wherein dispersing the plurality of diatom frustule portions in the dispersing solvent comprises obtaining a dispersion comprising about 1 weight percent to about 5 weight percent of the plurality of diatom frustule portions.

259. The method of any one of embodiments 214 to 258, wherein removing the organic contaminant comprises heating the plurality of diatom frustule portions in the presence of a bleach.

260. The method of embodiment 259, wherein the bleach comprises at least one of a hydrogen peroxide, and a nitric acid.

261. The method of embodiment 260, wherein heating comprises heating the plurality of diatom frustule portions in a solution comprising an amount of hydrogen peroxide in a range from about 10 volume percent to about 20 volume percent.

262. The method of any one of embodiments 259 to 261, wherein heating comprises heating the plurality of diatom frustule portions for a duration of about 5 minutes to about 15 minutes.

263. The method of any one of embodiments 214 to 262, wherein removing the organic contaminant comprises annealing the plurality of diatom frustule portions.

264. The method of any one of embodiments 214 to 263, wherein removing the inorganic contaminant comprises combining the plurality of diatom frustule portions with at least one of a hydrochloric acid and a sulfuric acid.

265. The method of embodiment 264, wherein combining comprises mixing the plurality of diatom frustule portions in a solution comprising about 15 volume percent to about 25 volume percent of hydrochloric acid.

266. The method of embodiment 265, wherein the mixing is for a duration of about 20 minutes to about 40 minutes.

267. A method of extracting a diatom frustule portion, the method comprising:

dispersing a plurality of diatom frustule portions with a surfactant, the surfactant reducing an agglomeration of the plurality of diatom frustule portions.

268. The method of embodiment 267, further comprising extracting a plurality of diatom frustule portions having at least one common characteristic using a disc stack centrifuge.

269. The method of embodiment 267 or 268, further comprising dispersing the plurality of diatom frustule portions in a dispersing solvent.

270. The method of any one of embodiments 267 to 269, further comprising removing at least one of an organic contaminant and an inorganic contaminant.

271. The method of any one of embodiments 267 to 270, wherein the at least one common characteristic comprises at least one of a dimension, a shape, a material, and a degree of brokenness.

272. The method of embodiment 271, wherein the dimension comprises at least one of a length and a diameter.

273. The method of any one of embodiments 267 to 272, wherein a solid mixture comprises the plurality of diatom frustule portions.

274. The method of embodiment 273, further comprising reducing a particle dimension of the solid mixture.

275. The method of embodiment 274, wherein reducing the particle dimension of the solid mixture is before dispersing the plurality of diatom frustule portions in the dispersing solvent.

276. The method of embodiment 274 or 275, wherein reducing the particle dimension comprises grinding the solid mixture.

277. The method of embodiment 276, wherein grinding the solid mixture comprises applying to the solid mixture at least one of a mortar and a pestle, a jar mill, and a rock crusher.

278. The method of any one of embodiments 273 to 277, further comprising extracting a component of the solid mixture having a longest component dimension that is greater than a longest frustule portion dimension of the plurality of diatom frustule portions.

279. The method of embodiment 278, wherein extracting the component of the solid mixture comprises sieving the solid mixture.

280. The method of embodiment 279, wherein sieving the solid mixture comprises processing the solid mixture with a sieve having a mesh size from about 15 microns to about 25 microns.

281. The method of embodiment 279, wherein sieving the solid mixture comprises processing the solid mixture with a sieve having a mesh size from about 10 microns to about 25 microns.

282. The method of any one of embodiments 267 to 281, further comprising sorting the plurality of diatom frustule portions to separate a first diatom frustule portion from a second diatom frustule portion, the first diatom frustule portion having a greater longest dimension.

283. The method of embodiment 282, wherein the first diatom frustule portion comprises a plurality of unbroken diatom frustule portions.

284. The method of embodiment 282 or 283, wherein the second diatom frustule portion comprises a plurality of broken diatom frustule portions.

285. The method of any one of embodiments 282 to 284, wherein sorting comprises filtering the plurality of diatom frustule portions.

286. The method of embodiment 285, wherein filtering comprises disturbing agglomeration of the plurality of diatom frustule portions.

287. The method of embodiment 286, wherein disturbing agglomeration of the plurality of diatom frustule portions comprises stirring.

288. The method of embodiment 286 or 287, wherein disturbing agglomeration of the plurality of diatom frustule portions comprises shaking.

289. The method of any one of embodiments 286 to 288, wherein disturbing agglomeration of the plurality of diatom frustule portions comprises bubbling.

290. The method of any one of embodiments 285 to 289, wherein filtering comprises applying a sieve to the plurality of diatom frustule portions.

291. The method of embodiment 290, wherein the sieve has a mesh size from about 5 microns to about 10 microns.

292. The method of embodiment 290, wherein the sieve has a mesh size of about 7 microns.

293. The method of any one of embodiments 267 to 292, further comprising obtaining a washed diatom frustule portion.

294. The method of embodiment 293, wherein obtaining the washed diatom frustule portion comprises washing the plurality of diatom frustule portions with a cleaning solvent after removing the at least one of the organic contaminant and the inorganic contaminant.

295. The method of embodiment 293 or 294 wherein obtaining the washed diatom frustule portion comprises washing the diatom frustule portion having the at least one common characteristic with a cleaning solvent.

296. The method of embodiment 294 or 295, further comprising removing the cleaning solvent.

297. The method of embodiment 296, wherein removing the cleaning solvent comprises sedimenting the plurality of diatom frustule portions after removing the at least one of the organic contaminant and the inorganic contaminant.

298. The method of embodiment 296 or 297, wherein removing the cleaning solvent comprises sedimenting the plurality of diatom frustule portions having the at least one common characteristic.

299. The method of embodiment 297 or 298, wherein sedimenting comprises centrifuging.

300. The method of embodiment 299, wherein centrifuging comprises applying a centrifuge suitable for large scale processing.

301. The method of embodiment 300, wherein centrifuging comprises applying at least one of a disc stack centrifuge, a decanter centrifuge, and a tubular bowl centrifuge.

302. The method of any one of embodiments 295 to 301, wherein at least one of the dispersing solvent and the cleaning solvent comprises water.

303. The method of any one of embodiments 269 to 302, wherein at least one of dispersing the plurality of diatom frustule portions in the dispersing solvent and dispersing the plurality of diatom frustule portions in the surfactant comprises sonicating the plurality of diatom frustules.

304. The method of any one of embodiments 267 to 303, wherein the surfactant comprises a cationic surfactant.

305. The method of embodiment 304, wherein the cationic surfactant comprises at least one of a benzalkonium chloride, a cetrimonium bromide, a lauryl methyl gluceth-10 hydroxypropyl dimonium chloride, a benzethonium chloride, a benzethonium chloride, a bronidox, a dmethyldioctadecylammonium chloride, and a tetramethylammonium hydroxide.

306. The method of any one of embodiments 267 to 305, wherein the surfactant comprises a non-ionic surfactant.

307. The method of embodiment 306, wherein the non-ionic surfactant comprises at least one of a cetyl alcohol, a stearyl alcohol, a cetostearyl alcohol, an oleyl alcohol, a polyoxyethylene glycol alkyl ether, an octaethylene glycol monododecyl ether, a glucoside alkyl ethers, a decyl glucoside, a polyoxyethylene glycol octylphenol ethers, an octylphenol ethoxylate (Triton X-100™), a nonoxynol-9, a glyceryl laurate, a polysorbate, and a poloxamer.

308. The method of any one of embodiments 267 to 307, further comprising dispersing the plurality of diatom frustules in an additive component.

309. The method of embodiment 308, wherein dispersing the plurality of diatom frustules in an additive component is before dispersing the plurality of diatom frustules in the surfactant.

310. The method of embodiment 308, wherein dispersing the plurality of diatom frustules in an additive component is after dispersing the plurality of diatom frustules in the surfactant.

311. The method of embodiment 308, wherein dispersing the plurality of diatom frustules in an additive component is at least partially simultaneous with dispersing the plurality of diatom frustules in the surfactant.

312. The method of any one of embodiments 308 to 311, wherein the additive component comprises at least one of a potassium chloride, an ammonium chloride, an ammonium hydroxide, and a sodium hydroxide.

313. The method of any one of embodiments 269 to 312, wherein dispersing the plurality of diatom frustule portions in the dispersing solvent comprises obtaining a dispersion comprising about 1 weight percent to about 5 weight percent of the plurality of diatom frustule portions.

314. The method of any one of embodiments 270 to 313, wherein removing the organic contaminant comprises heating the plurality of diatom frustule portions in the presence of a bleach.

315. The method of embodiment 314, wherein the bleach comprises at least one of a hydrogen peroxide, and a nitric acid.

316. The method of embodiment 315, wherein heating comprises heating the plurality of diatom frustule portions in

a solution comprising an amount of hydrogen peroxide in a range from about 10 volume percent to about 20 volume percent.

317. The method of any one of embodiments 314 to 316, wherein heating comprises heating the plurality of diatom frustule portions for a duration of about 5 minutes to about 15 minutes.

318. The method of any one of embodiments 270 to 317, wherein removing the organic contaminant comprises annealing the plurality of diatom frustule portions.

319. The method of any one of embodiments 270 to 218, wherein removing the inorganic contaminant comprises combining the plurality of diatom frustule portions with at least one of a hydrochloric acid and a sulfuric acid.

320. The method of embodiment 319, wherein combining comprises mixing the plurality of diatom frustule portions in a solution comprising about 15 volume percent to about 25 volume percent of hydrochloric acid.

321. The method of embodiment 320, wherein the mixing is for a duration of about 20 minutes to about 40 minutes.

322. A method of forming silver nanostructures on a diatom frustule portion, the method comprising:

forming a silver seed layer on a surface of the diatom frustule portion; and

forming a nanostructure on the seed layer.

323. The method of embodiment 322, wherein the nanostructures comprises at least one of a coating, a nanowire, a nanoplate, a dense array of nanoparticles, a nanobelt, and a nanodisk.

324. The method of embodiment 322 or 323, wherein the nanostructures comprises silver.

325. The method of any one of embodiment 322 to 324, wherein forming the silver seed layer comprises applying a cyclic heating regimen to a first silver contributing component and the diatom frustule portion.

326. The method of embodiment 325, wherein applying the cyclic heating regimen comprises applying a cyclic microwave power.

327. The method of embodiment 326, wherein applying the cyclic microwave power comprises alternating a microwave power between about 100 Watt and 500 Watt.

328. The method of embodiment 327, wherein alternating comprises alternating the microwave power every minute.

329. The method of embodiment 327 or 328, wherein alternating comprises alternating the microwave power for a duration of about 30 minutes.

330. The method of embodiment 327 or 328, wherein alternating comprises alternating the microwave power for a duration of about 20 minutes to about 40 minutes.

331. The method of any one of embodiments 322 to 330, wherein forming the silver seed layer comprises combining the diatom frustule portion with a seed layer solution.

332. The method of embodiment 331, wherein the seed layer solution comprises the first silver contributing component and a seed layer reducing agent.

333. The method of embodiment 332, wherein the seed layer reducing agent is a seed layer solvent.

334. The method of embodiment 333, wherein the seed layer reducing agent and the seed layer solvent comprises a polyethylene glycol.

335. The method of embodiment 331, wherein the seed layer solution comprises the first silver contributing component, a seed layer reducing agent and a seed layer solvent.

336. The method of any one of embodiments 331 to 335, wherein forming the silver seed layer further comprises mixing the diatom frustule portion with the seed layer solution.

337. The method of embodiment 336, wherein mixing comprises ultrasonicating.

338. The method of embodiment 337, wherein the seed layer reducing agent comprises a N,N-Dimethylformamide, the first silver contributing component comprises a silver nitrate, and the seed layer solvent comprises at least one of a water and a polyvinylpyrrolidone.

339. The method of any one of embodiments 322 to 338, wherein forming the nanostructure comprises combining the diatom frustule portion with a nanostructure forming reducing agent.

340. The method of embodiment 339, wherein forming the nanostructure further comprises heating the diatom frustule portion after combining the diatom frustule portion with the nanostructure forming reducing agent.

341. The method of embodiment 340, wherein heating comprises heating to a temperature of about 120° C. to about 160° C.

342. The method of embodiment 340 or 341, wherein forming the nanostructure further comprises titrating the diatom frustule portion with a titration solution comprising a nanostructure forming solvent and a second silver contributing component.

343. The method of embodiment 342, wherein forming the nanostructure further comprises mixing after titrating the diatom frustule portion with the titration solution.

344. The method of any one of embodiments 339 to 343, wherein at least one of the seed layer reducing agent and the nanostructure forming reducing agent comprises at least one of a hydrazine, a formaldehyde, a glucose, sodium tartrate, an oxalic acid, a formic acid, an ascorbic acid, and an ethylene glycol.

345. The method of any one of embodiments 342 to 344, wherein at least one of the first silver contributing component and the second silver contributing component comprises at least one of a silver salt and a silver oxide.

346. The method of embodiment 345, wherein the silver salt comprises at least one of a silver nitrate and an ammoniacal silver nitrate, a silver chloride (AgCl), a silver cyanide (AgCN), a silver tetrafluoroborate, a silver hexafluorophosphate, and a silver ethylsulphate.

347. The method of any one of embodiments 322 to 346, wherein forming the nanostructure is in an ambient to reduce oxide formation.

348. The method of embodiment 347, wherein the ambient comprises an argon atmosphere.

349. The method of any one of embodiments 342 to 348, wherein at least one of the seed layer solvent and the nanostructure forming solvent comprises at least one of a propylene glycol, a water, a methanol, an ethanol, a 1-propanol, a 2-propanol a 1-methoxy-2-propanol, a 1-butanol, a 2-butanol a 1-pentanol, a 2-pentanol, a 3-pentanol, a 1-hexanol, a 2-hexanol, a 3-hexanol, an octanol, a 1-octanol, a 2-octanol, a 3-octanol, a tetrahydrofurfuryl alcohol (THFA), a cyclohexanol, a cyclopentanol, a terpineol, a butyl lactone; a methyl ethyl ether, a diethyl ether, an ethyl propyl ether, a polyethers, a diketones, a cyclohexanone, a cyclopentanone, a cycloheptanone, a cyclooctanone, an acetone, a benzophenone, an acetylacetone, an acetophenone, a cyclopropanone, an isophorone, a methyl ethyl ketone, an ethyl acetate, a dimethyl adipate, a propylene glycol monomethyl ether acetate, a dimethyl glutarate, a dimethyl succinate, a glycerin acetate, a carboxylates, a propylene carbonate, a glycerin, a diol, a triol, a tetraol, a pentanol, an ethylene glycol, a diethylene glycol, a polyethylene glycol, a propylene glycol, a dipropylene glycol, a glycol ether, a glycol ether acetate, a 1,4-butanediol, a 1,2-butanediol, a 2,3-butanediol,

a 1,3-propanediol, a 1,4-butanediol, a 1,5-pentanediol, a 1,8-octanediol, a 1,2-propanediol, a 1,3-butanediol, a 1,2-pentanediol, an etohexadiol, a p-menthane-3,8-diol, a 2-methyl-2,4-pentanediol, a tetramethyl urea, a n-methylpyrrolidone, an acetonitrile, a tetrahydrofuran (THF), a dimethyl formamide (DMF), a N-methyl formamide (NMF), a dimethyl sulfoxide (DMSO), a thionyl chloride and a sulfuryl chloride.

350. The method of any one of embodiments 322 to 349, wherein the diatom frustule portion comprises a broken diatom frustule portion.

351. The method of any one of embodiments 322 to 349, wherein the diatom frustule portion comprises an unbroken diatom frustule portion.

352. The method of any one of embodiments 322 to 351, wherein the diatom frustule portion is obtained through a diatom frustule portion separation process.

353. The method of embodiment 352, wherein the process comprises at least one of using a surfactant to reduce an agglomeration of a plurality of diatom frustule portions and using a disc stack centrifuge.

354. A method of forming zinc-oxide nanostructures on a diatom frustule portion, the method comprising:

forming a zinc-oxide seed layer on a surface of the diatom frustule portion; and

forming a nanostructure on the zinc-oxide seed layer.

355. The method of embodiment 354, wherein the nanostructure comprises at least one of a nanowire, a nanoplate, a dense array of nanoparticles, a nanobelt, and a nanodisk.

356. The method of embodiment 354 or 355, wherein the nanostructures comprises zinc-oxide.

357. The method of any one of embodiments 354 to 356, wherein forming the zinc-oxide seed layer comprises heating a first zinc contributing component and the diatom frustule portion.

358. The method of embodiment 357, wherein heating the first zinc contributing component and the diatom frustule portion comprises heating to a temperature in a range from about 175° C. to about 225° C.

359. The method of any one of embodiments 354 to 358, wherein forming the nanostructure comprises applying a heating regimen to the diatom frustule portion having the zinc-oxide seed layer in the presence of a nanostructure forming solution comprising a second zinc contributing component.

360. The method of embodiment 359, wherein the heating regimen comprises heating to a nanostructure forming temperature.

361. The method of embodiment 360, wherein the nanostructure forming temperature is from about 80° C. to about 100° C.

362. The method of embodiment 360 or 361, wherein the heating is for a duration of about one to about three hours.

363. The method of any one of embodiments 359 to 362, wherein the heating regimen comprises applying a cyclic heating routine.

364. The method of embodiment 363, wherein the cyclic heating routine comprises applying a microwave heating to the diatom frustule portion having the zinc-oxide seed layer for a heating duration and then turning the microwaving heating off for a cooling duration, for a total cyclic heating duration.

365. The method of embodiment 364, wherein the heating duration is about 1 minute to about 5 minutes.

366. The method of embodiment 364 or 365, wherein the cooling duration is about 30 seconds to about 5 minutes.

367. The method of any one of embodiments 364 to 366, wherein the total cyclic heating duration is about 5 minutes to about 20 minutes.

368. The method of any one of embodiments 364 to 367, wherein applying the microwave heating comprises applying about 480 Watt to about 520 Watt of microwave power.

369. The method of any one of embodiments 364 to 367, wherein applying the microwave heating comprises applying about 80 Watt to about 120 Watt of microwave power.

370. The method of any one of embodiments 359 to 369, wherein at least one of the first zinc contributing component and the second zinc contributing component comprise at least one of a zinc acetate, a zinc acetate hydrate, a zinc nitrate, a zinc nitrate hexahydrate, a zinc chloride, a zinc sulfate, and a sodium zincate.

371. The method of any one of embodiments 359 to 370, wherein the nanostructure forming solution comprises a base.

372. The method of embodiment 371, wherein the base comprises at least one of a sodium hydroxide, an ammonium hydroxide, potassium hydroxide, a teramethylammonium hydroxide, a lithium hydroxide, a hexamethylenetetramine, an ammonia solution, a sodium carbonate, and a ethylenediamine.

373. The method of any one of embodiments 354 to 372, wherein forming the nanostructure further comprises adding an additive component.

374. The method of embodiment 373, wherein the additive component comprises at least one of a tributylamine, a triethylamine, a triethanolamine, a diisopropylamine, an ammonium phosphate, a 1,6-hexadianol, a triethyldiethylnol, an isopropylamine, a cyclohexylamine, a n-butylamine, an ammonium chloride, a hexamethylenetetramine, an ethylene glycol, an ethanoamine, a polyvinylalcohol, a polyethylene glycol, a sodium dodecyl sulphate, a cetyltrimethyl ammonium bromide, and a carbamide.

375. The method of any one of embodiments 359 to 374, wherein at least one of the nanostructure forming solution and a zinc-oxide seed layer forming solution comprises a solvent, the solvent comprising at least one of a propylene glycol, a water, a methanol, an ethanol, a 1-propanol, a 2-propanol a 1-methoxy-2-propanol, a 1-butanol, a 2-butanol a 1-pentanol, a 2-pentanol, a 3-pentanol, a 1-hexanol, a 2-hexanol, a 3-hexanol, an octanol, a 1-octanol, a 2-octanol, a 3-octanol, a tetrahydrofurfuryl alcohol (THFA), a cyclohexanol, a cyclopentanol, a terpineol, a butyl lactone; a methyl ethyl ether, a diethyl ether, an ethyl propyl ether, a polyethers, a diketones, a cyclohexanone, a cyclopentanone, a cycloheptanone, a cyclooctanone, an acetone, a benzophenone, an acetylacetone, an acetophenone, a cyclopropanone, an isophorone, a methyl ethyl ketone, an ethyl acetate, a dimethyl adipate, a propylene glycol monomethyl ether acetate, a dimethyl glutarate, a dimethyl succinate, a glycerin acetate, a carboxylates, a propylene carbonate, a glycerin, a diol, a triol, a tetraol, a pentanol, an ethylene glycol, a diethylene glycol, a polyethylene glycol, a propylene glycol, a dipropylene glycol, a glycol ether, a glycol ether acetate, a 1,4-butanediol, a 1,2-butanediol, a 2,3-butanediol, a 1,3-propanediol, a 1,4-butanediol, a 1,5-pentanediol, a 1,8-octanediol, a 1,2-propanediol, a 1,3-butanediol, a 1,2-pentanediol, an etohexadiol, a p-menthane-3,8-diol, a 2-methyl-2,4-pentanediol, a tetramethyl urea, a n-methylpyrrolidone, an acetonitrile, a tetrahydrofuran (THF), a dimethyl formamide (DMF), a N-methyl formamide (NMF), a dimethyl sulfoxide (DMSO), a thionyl chloride and a sulfuryl chloride.

376. The method of any one of embodiments 354 to 375, wherein the diatom frustule portion comprises a broken diatom frustule portion.

377. The method of any one of embodiments 354 to 375, wherein the diatom frustule portion comprises an unbroken diatom frustule portion.

378. The method of any one of embodiments 354 to 375, wherein the diatom frustule portion is obtained through a diatom frustule portion separation process.

379. The method of embodiment 378, wherein the process comprises at least one of using a surfactant to reduce an agglomeration of a plurality of diatom frustule portions and using a disc stack centrifuge.

380. A method of forming carbon nanostructures on a diatom frustule portion, the method comprising:

forming a metal seed layer on a surface of the diatom frustule portion; and

forming a carbon nanostructure on the seed layer.

381. The method of embodiment 380, wherein the carbon nanostructure comprises a carbon nanotube.

382. The method of embodiment 381, wherein the carbon nanotube comprise at least one of a single-walled carbon nanotube and a multi-walled carbon nanotube.

383. The method of any one of embodiments 380 to 382, wherein forming the metal seed layer comprises spray coating the surface of the diatom frustule portion.

384. The method of any one of embodiments 380 to 383, wherein forming the metal seed layer comprises introducing the surface of the diatom frustule portion to at least one of a liquid comprising the metal, a gas comprising the metal and the solid comprising a metal.

385. The method of any one of embodiments 380 to 384, wherein forming the carbon nanostructure comprises using chemical vapor deposition (CVD).

386. The method of any one of embodiments 380 to 385, wherein forming the carbon nanostructure comprises exposing the diatom frustule portion to a nanostructure forming reducing gas after exposing the diatom frustule portion to a nanostructure forming carbon gas.

387. The method of any one of embodiments 380 to 385, wherein forming the carbon nanostructure comprises exposing the diatom frustule portion to a nanostructure forming reducing gas before exposing the diatom frustule portion to a nanostructure forming carbon gas.

388. The method of any one of embodiments 380 to 385, wherein forming the carbon nanostructure comprises exposing the diatom frustule portion to a nanostructure forming gas mixture comprising a nanostructure forming reducing gas and a nanostructure forming carbon gas.

389. The method of embodiment 388, wherein the nanostructure forming gas mixture further comprises a neutral gas.

390. The method of embodiment 389, wherein the neutral gas comprises argon.

391. The method of any one of embodiments 380 to 390, wherein the metal comprises at least one of a nickel, an iron, a cobalt, a cobalt-molibdenium bimetallic, a copper, a gold, a silver, a platinum, a palladium, a manganese, an aluminum, a magnesium, a chromium, an antimony, an aluminum-iron-molybdenum (Al/Fe/Mo), an iron pentacarbonyl ($Fe(CO)_5$)), an iron (III) nitrate hexahydrate ($(Fe(NO_3)_3.6H_2O)$, a colbalt (II) chloride hexahydrate ($CoCl_2.6H_2O$), an ammonium molybdate tetrahydrate ($(NH_4)_6Mo_7O_{24}.4H_2O$), a molybdenum (VI) dichloride dioxide MoO_2Cl_2, and an alumina nanopowder.

392. The method of any one of embodiments 286 to 391, wherein the nanostructure forming reducing gas comprises at least one of an ammonia, a nitrogen, and a hydrogen.

393. The method of any one of embodiments 286 to 392, wherein the nanostructure forming carbon gas comprises at least one of an acetylene, an ethylene, an ethanol, a methane, a carbon oxide, and a benzene.

394. The method of any one of embodiments 380 to 393, wherein forming the metal seed layer comprises forming a silver seed layer.

395. The method of embodiment 394, wherein forming the silver seed layer comprises forming a silver nanostructure on the surface of the diatom frustule portion.

396. The method of any one of embodiments 380 to 395, wherein the diatom frustule portion comprises a broken diatom frustule portion.

397. The method of any one of embodiments 380 to 395, wherein the diatom frustule portion comprises an unbroken diatom frustule portion.

398. The method of any one of embodiments 380 to 397, wherein the diatom frustule portion is obtained through a diatom frustule portion separation process.

399. The method of embodiment 398, wherein the process comprises at least one of using a surfactant to reduce an agglomeration of a plurality of diatom frustule portions and using a disc stack centrifuge.

400. A method of fabricating a silver ink, the method comprising:

combining an ultraviolet light sensitive component and a plurality of diatom frustule portions having a silver nanostructure on a surface of the plurality of diatom frustule portions, the surface comprising a plurality of perforations.

401. The method of embodiment 400, further comprising forming a silver seed layer on the surface of the plurality of diatom frustule portions.

402. The method of embodiment 400 or 401, further comprising forming the silver nanostructure on the seed layer.

403. The method of any one of embodiments 400 to 402, wherein the plurality of diatom frustule portions comprises a plurality of broken diatom frustule portions.

404. The method of any one of embodiments 400 to 403, wherein the plurality of diatom frustule portions comprises a plurality of diatom frustule flakes.

405. The method of any one of embodiments 400 to 404, wherein the silver ink is depositable in a layer having a thickness of about 5 microns to about 15 microns after curing.

406. The method of any one of embodiments 400 to 405, wherein at least one of the plurality of perforations comprises a diameter of about 250 nanometers to about 350 nanometers.

407. The method of any one of embodiments 400 to 406, wherein the silver nanostructure comprises a thickness of about 10 nanometers to about 500 nanometers.

408. The method of any one of embodiments 400 to 407, wherein the silver ink comprises an amount of diatom frustules within a range of about 50 weight percent to about 80 weight percent.

409. The method of any one of embodiments 401 to 408, wherein forming the silver seed layer comprises forming the silver seed layer on a surface within the plurality of perforations to form a plurality of silver seed plated perforations.

410. The method of any one of embodiments 401 to 409, wherein forming the silver seed layer comprises forming the silver seed layer on substantially all surfaces of the plurality of diatom frustule portions.

411. The method of any one of embodiments 402 to 410, wherein forming the silver nanostructure comprises forming the silver nanostructure on a surface within the plurality of perforations to form a plurality of silver nanostructure plated perforations.

412. The method of any one of embodiments 402 to 411, wherein forming the silver nanostructure comprises forming the silver nanostructure on substantially all surfaces of the plurality of diatom frustule portions.

413. The method of any one of embodiments 400 to 412, wherein the ultraviolet light sensitive component is sensitive to an optical radiation having a wavelength shorter than a dimension of the plurality of perforations.

414. The method of any one of embodiments 411 to 413, wherein the ultraviolet light sensitive component is sensitive to an optical radiation having a wavelength shorter than a dimension of at least one of the plurality of silver seed plated perforations and the plurality of silver nanostructure plated perforations.

415. The method of any one of embodiments 400 to 414, wherein combining the plurality of diatom frustule portions with the ultraviolet light sensitive component comprises combining the plurality of diatom frustule portions with a photoinitiation synergist agent.

416. The method of embodiment 415, wherein the photoinitiation synergist agent comprises at least one of an ethoxylated hexanediol acrylate, a propoxylated hexanediol acrylate, an ethoxylated trimethylpropane triacrylate, a triallyl cyanurate and an acrylated amine.

417. The method of any one of embodiments 400 to 416, wherein combining the plurality of diatom frustule portions with the ultraviolet light sensitive component comprises combining the plurality of diatom frustule portions with a photoinitiator agent.

418. The method of embodiment 417, wherein the photoinitiator agent comprises at least one of a 2-methyl-1-(4-methylthio)phenyl-2-morpholinyl-1-propanon and an isopropyl thioxothanone.

419. The method of any one of embodiments 400 to 418, wherein combining the plurality of diatom frustule portions with the ultraviolet light sensitive component comprises combining the plurality of diatom frustule portions with a polar vinyl monomer.

420. The method of embodiment 419, wherein the polar vinyl monomer comprises at least one of a n-vinyl-pyrrolidone and a n-vinylcaprolactam.

421. The method of any one of embodiments 400 to 420, further comprising combining the plurality of diatom frustule portions with a rheology modifying agent.

422. The method of any one of embodiments 400 to 421, further comprising combining the plurality of diatom frustule portions with a crosslinking agent.

423. The method of any one of embodiments 400 to 422, further comprising combining the plurality of diatom frustule portions with a flow and level agent.

424. The method of any one of embodiments 400 to 423, further comprising combining the plurality of diatom frustule portions with at least one of an adhesion promoting agent, a wetting agent, and a viscosity reducing agent.

425. The method of any one of embodiments 400 to 424, wherein the silver nanostructure comprises at least one of a coating, a nanowire, a nanoplate, a dense array of nanoparticles, a nanobelt, and a nanodisk.

426. The method of any one of embodiment 401 to 425, wherein forming the silver seed layer comprises applying a cyclic heating regimen to a first silver contributing component and the plurality of diatom frustule portions.

427. The method of any one of embodiments 401 to 426, wherein forming the silver seed layer comprises combining the diatom frustule portion with a seed layer solution.

428. The method of embodiment 427, wherein the seed layer solution comprises the first silver contributing component and a seed layer reducing agent.

429. The method of any one of embodiments 402 to 428, wherein forming the silver nanostructure comprises combining the diatom frustule portion with a nanostructure forming reducing agent.

430. The method of embodiment 429, wherein forming the silver nanostructure further comprises heating the diatom frustule portion after combining the diatom frustule portion with the nanostructure forming reducing agent.

431. The method of any one of embodiments 402 to 430, wherein forming the silver nanostructure further comprises titrating the diatom frustule portion with a titration solution comprising a nanostructure forming solvent and a second silver contributing component.

432. The method of any one of embodiments 400 to 431, wherein the plurality of diatom frustule portions are obtained through a diatom frustule portion separation process.

433. The method of embodiment 432, wherein the process comprises at least one of using a surfactant to reduce an agglomeration of a plurality of diatom frustule portions and using a disc stack centrifuge.

434. A conductive silver ink comprising:

an ultraviolet light sensitive component; and

a plurality of diatom frustule portions having a silver nanostructure on a surface of the plurality of diatom frustule portions, the surface comprising a plurality of perforations.

435. The conductive silver ink of embodiment 434, wherein the plurality of diatom frustule portions comprises a plurality of broken diatom frustule portion.

436. The conductive silver ink of embodiment 434 or 435, wherein the plurality of diatom frustule portions comprises a plurality of diatom frustule flakes.

437. The conductive silver ink of any one of embodiments 434 to 436, wherein the silver ink is depositable in a layer having a thickness of about 5 microns to about 15 microns after curing.

438. The conductive silver ink of any one of embodiments 434 to 437, wherein at least one of the plurality of perforations comprises a diameter of about 250 nanometers to about 350 nanometers.

439. The conductive silver ink of any one of embodiments 434 to 438, wherein the silver nanostructure comprises a thickness of about 10 nanometers to about 500 nanometers.

440. The conductive silver ink of any one of embodiments 434 to 439, wherein the silver ink comprises an amount of diatom frustules within a range of about 50 weight percent to about 80 weight percent.

441. The conductive silver ink of any one of embodiments 434 to 440, wherein at least one of the plurality of perforations comprises a surface having a silver nanostructure.

442. The conductive silver ink of any one of embodiments 434 to 441, wherein at least one of the plurality of perforations comprises a surface having a silver seed layer.

443. The conductive silver ink of any one of embodiments 434 to 442, wherein substantially all surfaces of the plurality of diatom frustule portions comprises a silver nanostructure.

444. The conductive silver ink of any one of embodiments 434 to 443, wherein the ultraviolet light sensitive component is sensitive to an optical radiation having a wavelength shorter than a dimension of the plurality of perforations.

445. The conductive silver ink of any one of embodiments 434 to 444, wherein the conductive silver ink is curable by an ultraviolet radiation.

446. The conductive silver ink of embodiment 445, wherein the conductive silver ink is curable when deposited in a layer having a thickness of about 5 microns to about 15 microns after curing.

447. The conductive silver ink of embodiment 445 or 446, wherein the plurality of perforations has a dimension configured to allow the ultraviolet radiation to pass through the plurality of diatom frustule portions.

448. The conductive silver ink of any one of embodiments 434 to 447, wherein the conductive silver ink is thermally curable.

449. The conductive silver ink of any one of embodiments 434 to 448, wherein the ultraviolet light sensitive component comprises a photoinitiation synergist agent.

450. The conductive silver ink of embodiment 449, wherein the photoinitiation synergist agent comprises at least one of an ethoxylated hexanediol acrylate, a propoxylated hexanediol acrylate, an ethoxylated trimethylpropane triacrylate, a triallyl cyanurate and an acrylated amine.

451. The conductive silver ink of any one of embodiments 434 to 450, wherein the ultraviolet light sensitive component comprises a photoinitiator agent.

452. The conductive silver ink of embodiment 451, wherein the photoinitiator agent comprises at least one of a 2-methyl-1-(4-methylthio)phenyl-2-morpholinyl-1-propanon and an isopropyl thioxothanone.

453. The conductive silver ink of any one of embodiments 434 to 452, wherein the ultraviolet light sensitive component comprises a polar vinyl monomer.

454. The conductive silver ink of embodiment 453, wherein the polar vinyl monomer comprises at least one of a n-vinyl-pyrrolidone and a n-vinylcaprolactam.

455. The conductive silver ink of any one of embodiments 434 to 454, further comprising at least one of a rheology modifying agent, a crosslinking agent, a flow and level agent, an adhesion promoting agent, a wetting agent, and a viscosity reducing agent.

456. The conductive silver ink of any one of embodiments 434 to 455, wherein the silver nanostructure comprises at least one of a coating, a nanowire, a nanoplate, a dense array of nanoparticles, a nanobelt, and a nanodisk.

457. A method of fabricating a silver film, the method comprising:

curing a mixture comprising an ultraviolet light sensitive component and a plurality of diatom frustule portions having a silver nanostructure on a surface of the plurality of diatom frustule portions, the surface comprising a plurality of perforations.

458. The method of embodiment 457, further comprising forming a silver seed layer on the surface of the plurality of diatom frustule portions.

459. The method of embodiment 457 or 458, further comprising forming the silver nanostructure on the seed layer.

460. The method of any one of embodiments 457 to 459, further comprising combining the plurality of diatom frustule portions with the ultraviolet light sensitive component to form a silver ink.

461. The method of any one of embodiments 457 to 460, wherein the plurality of diatom frustule portions comprises a plurality of broken diatom frustule portions.

462. The method of any one of embodiments 457 to 461, wherein the plurality of diatom frustule portions comprises a plurality of diatom frustule flakes.

463. The method of any one of embodiments 460 to 462, wherein the silver ink is depositable in a layer having a thickness of about 5 microns to about 15 microns after curing.

464. The method of any one of embodiments 457 to 463, wherein at least one of the plurality of perforations comprises a diameter of about 250 nanometers to about 350 nanometers.

465. The method of any one of embodiments 457 to 464, wherein the silver nanostructure comprises a thickness of about 10 nanometers to about 500 nanometers.

466. The method of any one of embodiments 460 to 465, wherein the silver ink comprises an amount of diatom frustules within a range of about 50 weight percent to about 80 weight percent.

467. The method of any one of embodiments 458 to 466, wherein forming the silver seed layer comprises forming the silver seed layer on a surface within the plurality of perforations to form a plurality of silver seed plated perforations.

468. The method of any one of embodiments 458 to 467, wherein forming the silver seed layer comprises forming the silver seed layer on substantially all surfaces of the plurality of diatom frustule portions.

469. The method of any one of embodiments 459 to 468, wherein forming the silver nanostructure comprises forming the silver nanostructure on a surface within the plurality of perforations to form a plurality of silver nanostructure plated perforations.

470. The method of any one of embodiments 459 to 469, wherein forming the silver nanostructure comprises forming the silver nanostructure on substantially all surfaces of the plurality of diatom frustule portions.

471. The method of any one of embodiments 457 to 470, wherein curing the mixture comprises exposing the mixture to an ultraviolet light having a wavelength shorter than a dimension of the plurality of perforations.

472. The method of any one of embodiments 469 to 471, wherein curing the mixture comprises exposing the mixture to an ultraviolet light having a wavelength shorter than a dimension of at least one of the plurality of silver seed plated perforations and the plurality of silver nano structure plated perforations.

473. The method of any one of embodiments 457 to 472, wherein curing the mixture comprises thermally curing the mixture.

474. The method of any one of embodiments 457 to 473, wherein the ultraviolet light sensitive component is sensitive to an optical radiation having a wavelength shorter than a dimension of the plurality of perforations.

475. The method of any one of embodiments 469 to 474, wherein the ultraviolet light sensitive component is sensitive to an optical radiation having a wavelength shorter than a dimension of at least one of the plurality of silver seed plated perforations and the plurality of silver nanostructure plated perforations.

476. The method of any one of embodiments 460 to 475, wherein combining the plurality of diatom frustule portions with the ultraviolet light sensitive component comprises combining the plurality of diatom frustule portions with a photoinitiation synergist agent.

477. The method of embodiment 476, wherein the photoinitiation synergist agent comprises at least one of an ethoxylated hexanediol acrylate, a propoxylated hexanediol acrylate, an ethoxylated trimethylpropane triacrylate, a triallyl cyanurate and an acrylated amine.

478. The method of any one of embodiments 460 to 477, wherein combining the plurality of diatom frustule portions with the ultraviolet light sensitive component comprises combining the plurality of diatom frustule portions with a photoinitiator agent.

479. The method of embodiment 478, wherein the photoinitiator agent comprises at least one of a 2-methyl-1-(4-methylthio)phenyl-2-morpholinyl-1-propanon and an isopropyl thioxothanone.

480. The method of any one of embodiments 460 to 479, wherein combining the plurality of diatom frustule portions with the ultraviolet light sensitive component comprises combining the plurality of diatom frustule portions with a polar vinyl monomer.

481. The method of embodiment 480, wherein the polar vinyl monomer comprises at least one of a n-vinyl-pyrrolidone and a n-vinylcaprolactam.

482. The method of any one of embodiments 457 to 481, further comprising combining the plurality of diatom frustule portions with a rheology modifying agent.

483. The method of any one of embodiments 457 to 482, further comprising combining the plurality of diatom frustule portions with a crosslinking agent.

484. The method of any one of embodiments 457 to 483, further comprising combining the plurality of diatom frustule portions with a flow and level agent.

485. The method of any one of embodiments 457 to 484, further comprising combining the plurality of diatom frustule portions with at least one of an adhesion promoting agent, a wetting agent, and a viscosity reducing agent.

486. The method of any one of embodiments 457 to 485, wherein the silver nanostructure comprises at least one of a coating, a nanowire, a nanoplate, a dense array of nanoparticles, a nanobelt, and a nanodisk.

487. The method of any one of embodiment 458 to 486, wherein forming the silver seed layer comprises applying a cyclic heating regimen to a first silver contributing component and the plurality of diatom frustule portions.

488. The method of any one of embodiments 458 to 487, wherein forming the silver seed layer comprises combining the diatom frustule portion with a seed layer solution.

489. The method of embodiment 488, wherein the seed layer solution comprises the first silver contributing component and a seed layer reducing agent.

490. The method of any one of embodiments 459 to 489, wherein forming the silver nanostructure comprises combining the diatom frustule portion with a nanostructure forming reducing agent.

491. The method of embodiment 490, wherein forming the silver nanostructure further comprises heating the diatom frustule portion after combining the diatom frustule portion with the nanostructure forming reducing agent.

492. The method of any one of embodiments 459 to 491, wherein forming the silver nanostructure further comprises titrating the diatom frustule portion with a titration solution comprising a nanostructure forming solvent and a second silver contributing component.

493. The method of any one of embodiments 457 to 492, wherein the plurality of diatom frustule portions are obtained through a diatom frustule portion separation process.

494. The method of embodiment 493, wherein the process comprises at least one of using a surfactant to reduce an agglomeration of a plurality of diatom frustule portions and using a disc stack centrifuge.

495. A conductive silver film comprising:

a plurality of diatom frustule portions having a silver nanostructure on a surface of each of the plurality of diatom frustule portions, the surface comprising a plurality of perforations.

496. The conductive silver film of embodiment 495, wherein the plurality of diatom frustule portions comprises a plurality of broken diatom frustule portion.

497. The conductive silver film of embodiment 495 or 496, wherein the plurality of diatom frustule portions comprises a plurality of diatom frustule flakes.

498. The conductive silver film of any one of embodiments 495 to 497, wherein at least one of the plurality of perforations comprises a diameter of about 250 nanometers to about 350 nanometers.

499. The conductive silver film of any one of embodiments 495 to 498, wherein the silver nanostructure comprises a thickness of about 10 nanometers to about 500 nanometers.

500. The conductive silver film of any one of embodiments 495 to 499, wherein at least one of the plurality of perforations comprises a surface having a silver nanostructure.

501. The conductive silver film of any one of embodiments 495 to 500, wherein at least one of the plurality of perforations comprises a surface having a silver seed layer.

502. The conductive silver film of any one of embodiments 495 to 501, wherein substantially all surfaces of the plurality of diatom frustule portions comprises a silver nanostructure.

503. The conductive silver film of any one of embodiments 495 to 502, wherein the silver nanostructure comprises at least one of a coating, a nanowire, a nanoplate, a dense array of nanoparticles, a nanobelt, and a nanodisk.

504. The conductive silver film of any one of embodiments 495 to 503, further comprising a binder resin.

505. A printed energy storage device comprising:

a first electrode;

a second electrode; and

a separator between the first electrode and the second electrode, at least one of the first electrode and the second electrode including a plurality of frustules comprising manganese-containing nanostructures.

506. The device of embodiment 505, wherein the frustules have a substantially uniform property, the substantially uniform property including at least one of a frustule shape, a frustule dimension, a frustule porosity, a frustule mechanical strength, a frustule material, and a degree of brokenness of a frustule.

507. The device of embodiment 505 or 506, wherein the manganese-containing nanostructures comprise an oxide of manganese.

508. The device of embodiment 507, wherein the oxide of manganese comprises manganese(II,III) oxide.

509. The device of embodiment 507 or 508, wherein the oxide of manganese comprises manganese oxyhydroxide.

510. The device of any one of embodiments 505-509, wherein at least one of the first electrode and the second electrode comprises frustules comprising zinc-oxide nano structures.

511. The device of embodiment 510, wherein the zinc-oxide nanostructures comprise at least one of a nano-wire and a nano-plate.

512. The device of any one of embodiments 505-511, wherein the manganese-containing nanostructures cover substantially all surfaces of the frustules.

513. A membrane of an energy storage device, the membrane comprising frustules comprising manganese-containing nanostructures.

514. The membrane of embodiment 513, wherein the manganese-containing nanostructures comprise an oxide of manganese.

515. The membrane of embodiment 514, wherein the oxide of manganese comprises manganese(II,III) oxide.

516. The membrane of embodiment 514 or 515, wherein the oxide of manganese comprises manganese oxyhydroxide.

517. The membrane of any one of embodiments 513-516, wherein at least some of the manganese-containing nanostructures comprise a nano-fiber.

518. The membrane of any one of embodiments 513-517, wherein at least some of the manganese-containing nanostructures have a tetrahedral shape.

519. The membrane of any one of embodiments 513-518, wherein the energy storage device comprises a zinc-manganese battery.

520. An ink for a printed film, the ink comprising:

a solution; and

frustules comprising manganese-containing nanostructures dispersed in the solution.

521. The ink of embodiment 520, wherein the manganese-containing nanostructures comprise an oxide of manganese.

522. The ink of embodiment 520 or 521, wherein the manganese-containing nanostructures comprises at least one of MnO_2, MnO, Mn_2O_3, MnOOH, and Mn_3O_4.

523. The ink of any one of embodiments 520-522, wherein at least some of the manganese-containing nanostructures comprise a nano-fiber.

524. The ink of any one of embodiments 520-523, wherein at least some of the manganese-containing nanostructures have a tetrahedral shape.

525. A method of forming manganese-containing nanostructures on a diatom frustule portion, the method comprising:

adding the frustules to an oxygenated manganese acetate solution; and

heating the frustules and the oxygenated manganese acetate solution.

526. The method of embodiment 525, further comprising forming the oxygenated manganese acetate solution, wherein forming oxygenated manganese acetate solution comprises dissolving manganese(II) acetate in oxygenated water.

527. The method of embodiment 526, wherein concentration of the manganese(II) acetate in the oxygenated manganese acetate solution is between about 0.05 M and about 1.2 M.

528. The method of any one of embodiments 525-527, further comprising forming the oxygenated manganese acetate solution, wherein forming oxygenated manganese acetate solution comprises dissolving a manganese salt in oxygenated water.

529. The method of embodiment 528, further comprising adding an oxidizing agent to the oxygenated manganese acetate solution.

530. The method of embodiment 529, wherein the oxidizing agent comprises peroxide.

531. The method of any one of embodiments 526-530, further comprising forming the oxygenated water, wherein forming oxygenated water comprises bubbling oxygen gas into water.

532. The method of embodiment 531, wherein bubbling the oxygen gas into the water so for a duration of about 10 minutes to about 60 minutes.

533. The method of any one of embodiments 525-532, wherein a weight percentage of the frustules in the oxygenated manganese acetate solution is between about 0.01 wt % and about 1 wt %.

534. The method of any one of embodiments 525-533, further comprising thermally treating the frustules and the oxygenated manganese acetate solution.

535. The method of embodiment 534, wherein thermally treating the frustules and the oxygenated manganese acetate solution comprises using a thermal technique.

536. The method of embodiment 535, wherein using the thermal technique comprises maintaining the frustules and the oxygenated manganese acetate solution at a temperature for between about 15 hours and about 40 hours.

537. The method of embodiment 536, wherein the temperature is between about 50° C. and about 90° C.

538. The method of embodiment 535, wherein using the thermal technique comprises maintaining the frustules and the oxygenated manganese acetate solution at a temperature between about 50° C. and about 90° C.

539. The method of any one of embodiments 534-538, wherein thermally treating the frustules and the oxygenated manganese acetate solution comprises using a microwave technique.

540. The method of embodiment 539, wherein using the thermal technique comprises maintaining the frustules and the oxygenated manganese acetate solution at a temperature for between about 10 minutes and about 120 minutes.

541. The method of embodiment 540, wherein the temperature is between about 50° C. and about 150° C.

542. The method of embodiment 539, wherein using the thermal technique comprises maintaining the frustules and the oxygenated manganese acetate solution at a temperature between about 50° C. and about 150° C.

543. The method of any one of embodiments 525-542, wherein carbon-containing nanostructures cover some surfaces of the frustules.

544. The method of embodiment 543, wherein the carbon-containing nanostructures comprise carbon nanotubes.

545. The method of embodiment 543 or 544, wherein the carbon-containing nanostructures comprise carbon nano-onions.

546. The method of any one of embodiments 543-545, wherein the carbon-containing nanostructures comprise reduced graphene oxide.

547. The device of any one of embodiments 505-512, wherein the manganese-containing nanostructures cover some surfaces of the frustules and carbon-containing nanostructures cover other surfaces of the frustules, the manganese-containing nanostructures interspersed with the carbon-containing nanostructures.

548. The device of embodiment 547, wherein the carbon-containing nanostructures comprise carbon nanotubes.

549. The device of embodiment 547 or 548, wherein the carbon-containing nanostructures comprise carbon nano-onions.

550. The device of any one of embodiments 547-549, wherein the carbon-containing nanostructures comprise reduced graphene oxide.

551. The membrane of any one of embodiments 513-519, wherein the manganese-containing nanostructures cover some surfaces of the frustules and carbon-containing nanostructures cover other surfaces of the frustules, the manganese-containing nanostructures interspersed with the carbon-containing nanostructures.

552. The membrane of embodiment 551, wherein the carbon-containing nanostructures comprise carbon nanotubes.

553. The membrane of embodiment 551 or 552, wherein the carbon-containing nanostructures comprise carbon nano-onions.

554. The membrane of any one of embodiments 551-554, wherein the carbon-containing nanostructures comprise reduced graphene oxide.

555. The ink of any one of embodiments 520-524, wherein the manganese-containing nanostructures cover some surfaces of the frustules and carbon-containing nanostructures cover other surfaces of the frustules, the manganese-containing nanostructures interspersed with the carbon-containing nanostructures

556. The ink of embodiment 555, wherein the carbon-containing nanostructures comprise carbon nanotubes.

557. The ink of embodiment 555 or 556, wherein the carbon-containing nanostructures comprise carbon nano-onions.

558. The ink of any one of embodiments 555-557, wherein the carbon-containing nanostructures comprise reduced graphene oxide.

559. An energy storage device, comprising:

a cathode comprising a first plurality of frustules, wherein the first plurality of frustules comprises nanostructures comprising an oxide of manganese; and

an anode comprising a second plurality of frustules, wherein the second plurality of frustules comprises nanostructures comprising zinc oxide.

560. The energy storage device of embodiment 559, wherein the oxide of manganese comprises MnO.

561. The energy storage device of embodiment 559 or 560, wherein the oxide of manganese comprises Mn_3O_4.

562. The energy storage device of any one of embodiments 559 to 561, wherein the oxide of manganese comprises at least one of Mn_2O_3, and MnOOH.

563. The energy storage device of any one of embodiments 559 to 562, wherein at least one of the first plurality of frustules comprises about 5 weight % to about 95 weight % of the oxide of manganese.

564. The energy storage device of embodiment 563, wherein the at least one of the first plurality of frustules comprises about 75 weight % to about 95 weight % of the oxide of manganese.

565. The energy storage device of any one of embodiments 559 to 564, wherein at least one of the second plurality of frustules comprises about 5 weight % to about 95 weight % of the zinc oxide.

566. The energy storage device of embodiment 565, wherein the at least one of the second plurality of frustules comprises about 50 weight % to about 60 weight % of the zinc oxide.

567. The energy storage device of any one of embodiments 559 to 566, wherein the anode further comprises an electrolyte salt.

568. The energy storage device of embodiment 567, wherein the electrolyte salt comprises a zinc salt.

569. The energy storage device of any one of embodiments 559 to 568, wherein at least one of the cathode and the anode further comprises carbon nanotubes.

570. The energy storage device of any one of embodiments 559 to 569, wherein at least one of the cathode and the anode further comprises a conductive filler.

571. The energy storage device of embodiment 570, wherein the conductive filler comprises graphite.

572. The energy storage device of any one of embodiments 559 to 571, wherein at least one of the cathode and the anode further comprises an ionic liquid.

573. The energy storage device of any one of embodiments 559 to 572, wherein at least one of the cathode and the anode further comprises a binder.

574. The energy storage device of any one of embodiments 559 to 573, further comprising a separator between the cathode and the anode.

575. The energy storage device of embodiment 574, wherein the separator further comprises a third plurality of frustules.

576. The energy storage device of embodiment 575, wherein the third plurality of frustules comprises substantially no surface modifications.

577. The energy storage device of any one of embodiments 574 to 576, wherein the separator further comprises an electrolyte.

578. The energy storage device of embodiment 577, wherein the electrolyte comprises the ionic liquid.

579. The energy storage device of embodiment 577 or 578, wherein the electrolyte comprises the electrolyte salt.

580. The energy storage device of any one of embodiments 574 to 579, wherein the separator further comprises a polymer.

581. The energy storage device of any one of embodiments 559 to 580, further comprising a first current collector coupled to the cathode and a second current collector coupled to the anode.

582. The energy storage device of embodiment 581, wherein at least one of the first current collector and the second current collector comprises a conductive foil.

583. The energy storage device of embodiment 582, wherein the conductive foil comprises at least one of aluminum, copper, nickel, stainless steel, graphite, graphene and carbon nanotubes.

584. The energy storage device of embodiment 582 or 583, wherein at least one of the first current collector and the second current collector comprises a printed current collector.

585. The energy storage device of embodiment 584, wherein the printed current collector comprises at least one of aluminum, copper, nickel, silver, bismuth, conductive carbon, carbon nanotubes, graphene and graphite.

586. A frustule comprising a plurality of nanostructures on at least one surface, wherein the plurality of nanostructures comprises zinc oxide.

587. The frustule of embodiment 586, wherein the frustule comprises about 5 weight % to about 95 weight % of the plurality of nanostructures comprising zinc oxide.

588. The frustule of embodiment 587, wherein the frustule comprises about 50 weight % to about 60 weight % of the nanostructures comprising zinc oxide.

589. The frustule of any one of embodiments 586 to 588, wherein the plurality of nanostructures comprises at least one of nanowires, nanoplates, dense nanoparticles, nanobelts, and nanodisks.

590. A frustule comprising a plurality of nanostructures on at least one surface, wherein the plurality of nanostructures comprises an oxide of manganese.

591. The frustule of embodiment 590, wherein the frustule comprises about 5 weight % to about 95 weight % of the plurality of nanostructures comprising the oxide of manganese.

592. The frustule of embodiment 591, wherein the frustule comprises about 75 weight % to about 95 weight % of the plurality of nanostructures comprising the oxide of manganese.

593. The frustule of any one of embodiments 590 to 592, wherein the oxide of manganese comprises MnO.

594. The frustule of any one of embodiments 590 to 593, wherein the oxide of manganese comprises Mn_3O_4.

595. The frustule of any one of embodiments 590 to 594, wherein the oxide of manganese comprises at least one of Mn_2O_3 and MnOOH.

596. The frustule of any one of embodiments 590 to 595, wherein the plurality of nanostructures comprises at least one of nanowires, nanoplates, dense nanoparticles, nanobelts, and nanodisks.

597. The frustule of any one of embodiments 590 to 596, wherein the plurality of nanostructures comprises at least one of nano-fibers and tetrahedral-shaped nanocrystals.

598. An electrode of an energy storage device, comprising:

a plurality of frustules, wherein each of the plurality of frustules comprises a plurality of nanostructures formed on at least one surface.

599. The electrode of embodiment 598, wherein the electrode is an anode of the energy storage device.

600. The electrode of embodiment 599, wherein the anode further comprises an electrolyte salt.

601. The electrode of embodiment 600, wherein the electrolyte salt comprises a zinc salt.

602. The electrode of any one of embodiments 599 to 601, wherein the plurality of nanostructures comprises zinc oxide.

603. The electrode of any one of embodiments 599 to 602, wherein the plurality of nanostructures comprises at least one of nanowires, nanoplates, dense nanoparticles, nanobelts, and nanodisks.

604. The electrode of any one of embodiments 599 to 603, wherein at least one of the plurality of frustules comprises about 5 weight % to about 95 weight % of the plurality of nano structures.

605. The electrode of embodiment 604, wherein the at least one of the plurality of frustules comprises about 50 weight % to about 60 weight % of the plurality of nano structures.

606. The electrode of embodiment 598, wherein the electrode is a cathode of the energy storage device.

607. The electrode of embodiment 606, wherein the plurality of nanostructures comprises an oxide of manganese.

608. The electrode of embodiment 607, wherein the oxide of manganese comprises MnO.

609. The electrode of embodiment 607 or 608, wherein the oxide of manganese comprises Mn_3O_4.

610. The electrode of any one of embodiments 607 to 609, wherein the oxide of manganese comprises at least one of Mn_2O_3 and MnOOH.

611. The electrode of any one of embodiments 606 to 610, wherein the plurality of nanostructures comprises at least one of nanowires, nanoplates, dense nanoparticles, nanobelts, and nanodisks.

612. The electrode of any one of embodiments 606 to 611, wherein the plurality of nanostructures comprises at least one of nano-fibers and tetrahedral-shaped nanocrystals.

613. The electrode of any one of embodiments 606 to 611, wherein at least one of the plurality of frustules comprises about 5 weight % to about 95 weight % of the plurality of nano structures.

614. The electrode of embodiment 613, wherein the at least one of the plurality of frustules comprises about 75 weight % to about 95 weight % of the plurality of nano structures.

615. The electrode of any one of embodiments 598 to 614, wherein the electrode further comprises carbon nanotubes.

616. The electrode of any one of embodiments 598 to 615, wherein the electrode further comprises a conductive filler.

617. The electrode of embodiment 616, wherein the conductive filler comprises graphite.

618. The electrode of any one of embodiments 598 to 617, wherein the electrode further comprises an ionic liquid.

619. The electrode of any one of embodiments 598 to 618, wherein the electrode further comprises a binder.

620. A method of forming zinc oxide nanostructures on a plurality of frustules, comprising:

providing the plurality of frustules;

forming a seed layer comprising zinc oxide on the plurality of frustules to provide a plurality of zinc oxide seeded frustules; and

forming nanostructures comprising zinc oxide on the seed layer of the plurality of zinc oxide seeded frustules.

621. The method of embodiment 620, wherein forming the seed layer comprises providing a seed layer solution comprising about 2 weight % to about 5 weight % of the plurality of frustules.

622. The method of embodiment 621, wherein the seed layer solution comprises about 0.1 weight % to about 0.5 weight % zinc salt.

623. The method of embodiment 622, wherein the zinc salt comprises $Zn(CH_3COO)_2$.

624. The method of any one of embodiments 621 to 623, wherein the seed layer solution comprises about 94.5 weight % to about 97.9 weight % of an alcohol.

625. The method of embodiment 624, wherein the alcohol comprises ethanol.

626. The method of any one of embodiments 621 to 625, further comprising heating the seed layer solution.

627. The method of embodiment 626, wherein heating the seed layer solution comprises heating the seed layer solution to a temperature greater than about 80° C.

628. The method of embodiment 626 or 627, wherein heating the seed layer solution comprises heating the seed layer solution in a vacuum oven.

629. The method of embodiment 628, wherein heating the seed layer solution in a vacuum oven comprises heating at a pressure of about 1 millibar.

630. The method of any one of embodiments 621 to 629, further comprising annealing the plurality of frustules.

631. The method of embodiment 631, wherein annealing comprises annealing at a temperature of about 200° C. to about 500° C.

632. The method of any one of embodiments 620 to 631, wherein forming the zinc oxide nanostructures comprises forming a nanostructure solution comprising about 1 weight % to about 5 weight % of the plurality of zinc oxide seeded frustules.

633. The method of embodiment 632, wherein the nanostructure solution comprises about 6 weight % to about 10 weight % of a zinc salt.

634. The method of embodiment 633, wherein the zinc salt comprises $Zn(NO_3)_2$.

635. The method of any one of embodiments 632 to 634, wherein the nanostructure solution comprises about 1 weight % to about 2 weight % of a base.

636. The method of embodiment 635, wherein the base comprises ammonium hydroxide (NH_4OH).

637. The method of any one of embodiments 632 to 636, wherein the nanostructure solution comprises about 1 weight % to about 5 weight % of an additive.

638. The method of embodiment 637, wherein the additive comprises hexamethylenetetramine (HMTA).

639. The method of any one of embodiments 632 to 638, wherein the nanostructure solution comprises about 78 weight % to about 91 weight % purified water.

640. The method of any one of embodiments 632 to 638, wherein forming the zinc oxide nanostructures comprises heating the nanostructure solution.

641. The method of embodiment 640, wherein heating comprises heating with a microwave.

642. The method of embodiment 640 or 641, wherein heating comprises heating to a temperature of about 100° C. to about 250° C.

643. The method of any one of embodiments 640 to 642, further comprising stirring during heating.

644. The method of any one of embodiments 620 to 643, wherein at least one of the plurality of frustules comprises about 5 weight % to about 95 weight % of the zinc oxide.

645. A method of forming nanostructures comprising an oxide of manganese on a plurality of frustules, comprising:

providing the plurality of frustules; and

forming the nanostructures comprising the oxide of manganese on the plurality of frustules, wherein forming the nanostructures comprises providing a solution comprising a manganese source for forming the nanostructures comprising the oxide of manganese.

646. The method of embodiment 645, wherein the manganese source comprises a manganese salt, and wherein the solution comprises about 7 weight % to about 10 weight % of the manganese salt.

647. The method of embodiment 646, wherein the manganese salt comprises manganese acetate ($Mn(CH_3COO)_2$).

648. The method of any one of embodiments 645 to 647, wherein the solution comprises about 0.5 weight % to about 2 weight % of the plurality of frustules.

649. The method of any one of embodiments 645 to 648, wherein the solution comprises about 5 weight % to about 10 weight % of a base.

650. The method of embodiment 649, wherein the base comprises ammonium hydroxide (NH_4OH).

651. The method of any one of embodiments 645 to 650, wherein the solution comprises about 78 weight % to about 87.5 weight % of oxygenated purified water.

652. The method of any one of embodiments 645 to 651, further comprising heating the solution.

653. The method of embodiment 652, wherein heating comprises heating with microwave.

654. The method of embodiment 652 or 653, wherein heating the solution comprises heating to a temperature of about 100° C. to about 250° C.

655. The method of any one of embodiments 652 to 654, further comprising stirring while heating.

656. An ink for an electrode of an energy storage device, comprising:

a plurality of frustules, wherein each of the plurality of frustules comprises a plurality of nanostructures formed on a surface; and

a polymer binder.

657. The ink of embodiment 656, wherein the electrode is an anode of the energy storage device.

658. The ink of embodiment 657, wherein the plurality of nanostructures comprises zinc oxide.

659. The ink of embodiment 657 or 658, wherein at least one of the plurality of frustules comprises about 5 weight % to about 95 weight % of the nanostructures.

660. The ink of any one of embodiments 657 to 659, further comprising an electrolyte salt.

661. The ink of embodiment 660, wherein the electrolyte salt comprises a zinc salt.

662. The ink of embodiment 661, wherein the zinc salt comprises zinc tetrafluoroborate.

663. The ink of embodiment 656, wherein the electrode is a cathode of the energy storage device.

664. The ink of embodiment 663, wherein the plurality of nanostructures comprises an oxide of manganese.

665. The ink of embodiment 664, wherein the oxide of manganese comprises MnO.

666. The ink of embodiment 664 or 665, wherein the oxide of manganese comprises Mn_3O_4.

667. The ink of any one of embodiments 663 to 666, wherein the oxide of manganese comprises at least one of Mn_2O_3 and MnOOH.

668. The ink of any one of embodiments 663 to 667, wherein at least one of the plurality of frustules comprises about 5 weight % to about 95 weight % of the nanostructures.

669. The ink of any one of embodiments of 656 to 668, further comprising about 10 weight % to about 20 weight % of the plurality of frustules.

670. The ink of any one of embodiments 656 to 669, further comprising an ionic liquid.

671. The ink of embodiment 670, wherein the ink comprises about 2 weight % to about 15 weight % of the ionic liquid.

672. The ink of embodiment 670 or 671, wherein the ionic liquid comprises 1-ethyl-3-ethylimidazolium tetrafluoroborate.

673. The ink of any one of embodiments of 656 to 672, further comprising a conductive filler.

674. The ink of embodiment 673, further comprising up to about 10 weight % of the conductive filler.

675. The ink of embodiment 673 or 674, wherein the conductive filler comprises graphite.

676. The ink of any one of embodiments of 656 to 675, further comprising carbon nanotubes.

677. The ink of embodiment 676, further comprising about 0.2 weight % to about 20 weight % of the carbon nanotubes.

678. The ink of embodiment 676 or 677, wherein the carbon nanotubes comprises multi-wall carbon nanotubes.

679. The ink of any one of embodiments of 656 to 678, wherein the ink comprises about 1 weight % to about 5 weight % of the polymer binder.

680. The ink of embodiment 679, wherein the polymer binder comprises polyvinylidene fluoride.

681. The ink of any one of embodiments of 656 to 680, further comprising a solvent.

682. The ink of embodiment 681, wherein the ink comprises about 47 weight % to about 86.8 weight % of the solvent.

683. The ink of embodiment 681 or 682, wherein the solvent comprises N-Methyl-2-pyrrolidone.

684. A method of preparing an ink for an electrode of an energy storage device, the method comprising:

providing an ionic liquid;

dispersing a plurality of carbon nanotubes in the ionic liquid to form a first dispersion comprising the plurality of carbon nanotubes and the ionic liquid; and

adding a plurality of frustules, wherein each of the plurality of frustules comprises a plurality of nanostructures on a surface.

685. The method of embodiment 684, wherein the plurality of nanostructures comprises zinc oxide.

686. The method of embodiment 684, wherein the plurality of nanostructures comprises an oxide of manganese.

687. The method of embodiment 686, wherein the oxide of manganese comprises MnO.

688. The method of embodiment 686 or 687, wherein the oxide of manganese comprises Mn_3O_4.

689. The method of any one of embodiments 686 to 688, wherein the oxide of manganese comprises at least one of Mn_2O_3 and MnOOH.

690. The method of any one of embodiments 684 to 689, further comprising forming a second dispersion comprising the plurality of carbon nanotubes, the ionic liquid and a solvent.

691. The method of embodiment 690, wherein the solvent comprises N-Methyl-2-pyrrolidone.

692. The method of embodiment 690 or 691, wherein adding the plurality of frustules comprises adding the plurality of frustules to the second dispersion to form a first mixture.

693. The method of embodiment 692, further comprising adding a conductive filler to the second dispersion to form the first mixture.

694. The method of embodiment 693, wherein the conductive filler comprises graphite.

695. The method of embodiment 692 or 693, further comprising adding an electrolyte salt to the first mixture to form a second mixture.

696. The method of embodiment 695, wherein the electrolyte salt comprises a zinc salt.

697. The method of embodiment 696, wherein the zinc salt comprises zinc tetrafluoroborate.

698. The method of any one of embodiments 695 to 697, wherein at least one of adding the plurality of frustules, the conductive filler and the electrolyte salt comprises stirring.

699. The method of embodiment 698, wherein stirring comprises applying a centrifugal mixer.

700. The method of any one of embodiments 695 to 699, further comprising adding a solution to the second mixture to form a third mixture, wherein the solution comprises the solvent and a polymer binder.

701. The method of embodiment 700, wherein the polymer binder is about 10 weight % to about 20 weight % of the solution.

702. The method of embodiment 700 or 701, wherein the polymer binder comprises polyvinylidene fluoride.

703. The method of any one of embodiments 700 to 702, further comprising heating the third mixture.

704. The method of embodiment 703, wherein the heating comprises heating to a temperature of about 80° C. to about 180° C.

705. The method of embodiment 703 or 704, further comprising stirring during the heating.

706. A method of printing an energy storage device, comprising:

printing a first electrode comprising a first plurality of frustules, wherein each of the plurality of frustules comprises a first plurality of nanostructures on a surface; and

printing a separator over the first electrode.

707. The method of embodiment 706, further comprising providing a first current collector, and wherein printing the first electrode comprises printing the first electrode over the first current collector.

708. The method of embodiment 707, wherein providing the first current collector comprises providing a first conductive foil.

709. The method of any one of embodiments 706 to 708, further comprising providing a second current collector.

710. The method of embodiment 709, wherein providing the second current collector comprises providing a second conductive foil.

711. The method of embodiment 710, further comprising printing a second electrode, wherein the second electrode comprises a second plurality of frustules, wherein each of the second plurality of frustules comprises a second plurality of nanostructures on a surface.

712. The method of embodiment 711, wherein printing the second electrode comprises printing the second electrode over the separator.

713. The method of embodiment 711, wherein printing the second electrode comprises printing the second electrode over the second current collector.

714. The method embodiment 713, further comprising printing the separator over the second electrode.

715. The method of embodiment 707, wherein providing the first current collector comprises printing the first current collector.

716. The method of embodiment 715, further comprising printing a second electrode over the separator, wherein the second electrode comprises a second plurality of frustules, wherein each of the second plurality of frustules comprises a second plurality of nanostructures on a surface.

717. The method of embodiment 716, further comprising printing a second current collector over the second electrode.

718. The method of embodiment 715, wherein further comprising printing a second current collector at a lateral distance from the first current collector.

719. The method of embodiment 718, further comprising printing a second electrode over the second current collector at the lateral distance from the first current collector, wherein the second electrode comprises a second plurality of frustules, wherein each of the second plurality of frustules comprises a second plurality of nanostructures on a surface.

720. The method of embodiment 719, wherein printing the separator comprises printing the separator over the first electrode and the second electrode.

721. A method of fabricating an energy storage device, comprising:

forming a first structure, wherein forming the first structure comprises:

printing a first electrode over a first current collector, and

printing a separator over the first electrode;

forming a second structure, wherein forming the second structure comprises:

printing a second electrode over a second current collector; and

coupling the first structure to the second structure to form the energy storage device,

wherein coupling comprises providing the separator between the first electrode and the second electrode.

722. A method of fabricating an energy storage device, comprising:

forming a first structure, wherein forming the first structure comprises:

printing a first electrode over a first current collector, and

printing a first portion of a separator over the first electrode;

forming a second structure, wherein forming the second structure comprises:

printing a second electrode over a second current collector, and

printing a second portion of the separator over the second electrode; and

coupling the first structure to the second structure to form the energy storage device,

wherein coupling comprises providing the first portion of the separator and the second portion of the separator between the first electrode and the second electrode.

723. A method of fabricating an energy storage device, comprising:

forming a first structure, wherein forming the first structure comprises:

printing a first electrode over a first current collector,

printing a separator over the first electrode, and

printing a second electrode on the separator;

forming a second structure, wherein forming the second structure comprises providing a second current collector; and

coupling the first structure to the second structure to form the energy storage device,

wherein coupling comprises providing the second electrode between the second current collector and the separator.

724. The method of any one of Embodiments 721-723, wherein the first current collector comprises a conductive foil.

725. The method of any one of Embodiments 721-723, further comprising forming the first current collector on a substrate.

726. The method of Embodiment 725, wherein forming the first current collector comprises printing the first current collector over the substrate.

727. The method of any one of Embodiments 721-726, wherein the second current collector comprises a conductive foil.

728. The method of any one of Embodiments 721-726, further comprising forming the second current collector on a second substrate.

729. The method of Embodiment 728, wherein forming the first current collector comprises printing the first current collector over the second substrate.

730. A method of fabricating an energy storage device, comprising:

printing a first current collector;

printing a first electrode over the first current collector;

printing a separator over the first electrode;

printing a second electrode over the separator; and

printing a second current collector over the second electrode.

731. A method of fabricating an energy storage device, comprising:

printing a first current collector;

printing a second current collector at a lateral distance from the first current collector;

printing a first electrode over the first current collector;

printing a second electrode over the second current collector; and

printing a separator over the first electrode and the second electrode and between the first electrode and the second electrode.

732. The method of any one of embodiments 721 to 731, wherein the first electrode comprises a first plurality of frustules, wherein each of the first plurality of frustules comprises nanostructures formed on at least one surface.

733. The method of embodiment 732, wherein the nanostructures comprise an oxide of manganese

734. The method of embodiment 733, wherein the oxide of manganese comprises MnO.

735. The method of embodiment 733 or 734, wherein the oxide of manganese comprises Mn_3O_4.

736. The method of any one of embodiments 733 to 735, wherein the oxide of manganese comprises at least one of Mn_2O_3 and MnOOH.

737. The method of any one of embodiments 721 to 736, wherein the second electrode comprises a second plurality of frustules, wherein each of the second plurality of frustules comprises nanostructures.

738. The method of embodiment 737, wherein the nanostructures comprise zinc oxide.

739. The method of any one of embodiments 721 to 738, wherein the separator comprises a third plurality of frustules, wherein each of the third plurality of frustules comprises substantially no surface modifications.

740. An energy storage device comprising:

a cathode comprising a first plurality of frustules, the first plurality of frustules comprises nanostructures comprising an oxide of manganese; and

an anode comprising a second plurality of frustules, the second plurality of frustules comprises nanostructures comprising zinc oxide.

741. The energy storage device of embodiment 740, wherein the oxide of manganese comprises MnO.

742. The energy storage device of embodiment 740 or 741, wherein the oxide of manganese comprises at least one of Mn_3O_4, Mn_2O_3, and MnOOH.

743. The energy storage device of any one of embodiments 740 to 742, wherein at least one of the first plurality of frustules comprises a ratio of a mass of the oxide of manganese to a mass of the at least one frustule of about 1:20 to about 20:1.

744. The energy storage device of any one of embodiments 740 to 743, wherein at least one of the second plurality of frustules comprises a ratio of a mass of the zinc oxide to a mass of the at least one frustule of about 1:20 to about 20:1.

745. The energy storage device of any one of embodiments 740 to 744, wherein the anode further comprises an electrolyte salt.

746. The energy storage device of embodiment 745, wherein the electrolyte salt comprises a zinc salt.

747. The energy storage device of any one of embodiments 740 to 746, wherein at least one of the cathode and the anode further comprises carbon nanotubes.

748. The energy storage device of any one of embodiments 740 to 747, wherein at least one of the cathode and the anode further comprises a conductive filler.

749. The energy storage device of embodiment 748, wherein the conductive filler comprises graphite.

750. The energy storage device of any one of embodiments 740 to 749, further comprising a separator between the cathode and the anode, wherein the separator comprises a third plurality of frustules.

751. The energy storage device of embodiment 750, wherein the third plurality of frustules comprises substantially no surface modifications.

752. The energy storage device of embodiment 750 or 751, wherein at least one of the cathode, the anode, and the separator comprises an ionic liquid.

753. The energy storage device of any one of embodiments 740 to 752, wherein the device is a rechargeable battery.

754. The energy storage device of any one of embodiments 740 to 753, wherein the first plurality of frustules comprises a first plurality of pores substantially not occluded by the nanostructures comprising the oxide of manganese, and wherein the second plurality of frustules comprises a second plurality of pores substantially not occluded by the nanostructures comprising the zinc oxide.

755. A frustule comprising a plurality of nanostructures on at least one surface, wherein the plurality of nanostructures comprises zinc oxide, wherein a ratio of a mass of the plurality of nanostructures to a mass of the frustule is about 1:1 to about 20:1.

756. The frustule of embodiment 755, wherein the plurality of nanostructures comprises at least one of nanowires, nanoplates, dense nanoparticles, nanobelts, and nanodisks.

757. The frustule of embodiment 755 or 756, wherein the frustule comprises a plurality of pores substantially not occluded by the plurality of nanostructures.

758. A frustule comprising a plurality of nanostructures on at least one surface, wherein the plurality of nanostructures comprises an oxide of manganese, wherein a ratio of a mass of the plurality of nanostructures to a mass of the frustule is about 1:1 to about 20:1.

759. The frustule of embodiment 758, wherein the oxide of manganese comprises MnO.

760. The frustule of embodiment 758 or 759, wherein the oxide of manganese comprises Mn_3O_4.

761. The frustule of any one of embodiments 758 to 760, wherein the oxide of manganese comprises at least one of Mn_2O_3 and MnOOH.

762. The frustule of any one of embodiments 758 to 761, wherein the plurality of nanostructures comprises at least one of nanowires, nanoplates, dense nanoparticles, nanobelts, and nanodisks.

763. The frustule of any one of embodiments 758 to 762, wherein the frustule comprises a plurality of pores substantially not occluded by the plurality of nanostructures.

764. An electrode of an energy storage device, the electrode comprising:

a plurality of frustules, wherein each of the plurality of frustules comprises a plurality of nanostructures formed on at least one surface, wherein at least one of the plurality of frustules comprises a ratio of a mass of the plurality of nanostructures to a mass of the at least one frustule of 1:20 to 20:1.

765. The electrode of embodiment 764, wherein the electrode is an anode of the energy storage device.

766. The electrode of embodiment 765, wherein the anode further comprises an electrolyte salt.

767. The electrode of embodiment 766, wherein the electrolyte salt comprises a zinc salt.

768. The electrode of any one of embodiments 765 to 767, wherein the plurality of nanostructures comprises zinc oxide.

769. The electrode of any one of embodiments 764 to 768, wherein the plurality of nanostructures comprises at least one of nanowires, nanoplates, dense nanoparticles, nanobelts, and nanodisks.

770. The electrode of embodiment 764 or 769, wherein the electrode is a cathode of the energy storage device.

771. The electrode of embodiment 770, wherein the plurality of nanostructures comprises an oxide of manganese.

772. The electrode of embodiment 771, wherein the oxide of manganese comprises MnO.

773. The electrode of embodiment 771 or 772, wherein the oxide of manganese comprises at least one of Mn_3O_4, Mn_2O_3 and MnOOH.

774. The electrode of any one of embodiments 764 to 773, further comprising carbon nanotubes.

775. The electrode of any one of embodiments 764 to 774, further comprising a conductive filler.

776. The electrode of embodiment 775, wherein the conductive filler comprises graphite.

777. The electrode of any one of embodiments 764 to 776, further comprising an ionic liquid.

778. The electrode of any one of embodiments 764 to 777, wherein each of the plurality of frustules comprises a plurality of pores substantially not occluded by the plurality of nano structures.

779. The energy storage device of any one of embodiments 559 to 562 and 565 to 585, wherein a mass of the nanostructures comprising the oxide of manganese of at least one frustule of the first plurality of frustules to a mass of the at least one frustule is about 1:20 to about 100:1.

780. The energy storage device of embodiment 779, wherein the mass of the nanostructures comprising the oxide of manganese of at least one frustule of the first plurality of frustules to the mass of the at least one frustule is about 1:1 to about 100:1.

781. The energy storage device of embodiment 779, wherein the mass of the nanostructures comprising the oxide of manganese of at least one frustule of the first plurality of frustules to the mass of the at least one frustule is about 1:20 to about 100:1.

782. The energy storage device of any one of embodiments 559 to 564, 567 to 585 and 779 to 781, wherein a mass of the ZnO of at least one frustule of the second plurality of frustules to a mass of the at least one frustule of the second plurality of frustules is about 1:20 to about 100:1.

783. The energy storage device embodiment 782, wherein the mass of the ZnO of at least one frustule of the second plurality of frustules to the mass of the at least one frustule of the second plurality of frustules is about 1:1 to about 100:1.

784. The energy storage device embodiment 782, wherein the mass of the ZnO of at least one frustule of the second plurality of frustules to the mass of the at least one frustule of the second plurality of frustules is about 20:1 to about 100:1.

785. The frustule of any one of embodiments 586 and 589, wherein a mass of the ZnO to a mass of the frustule is about 1:20 to about 100:1.

786. The frustule of embodiment 785, wherein the mass of the ZnO to the mass of the frustule is about 1:1 to about 100:1.

787. The frustule of embodiment 785, wherein the mass of the ZnO to the mass of the frustule is about 20:1 to about 100:1.

788. The frustule of any one of embodiments 590 and 593 to 597, wherein a mass of the plurality of nanostructures comprising the oxide of manganese to a mass of the frustule is about 1:20 to about 100:1.

789. The frustule of embodiment 788, wherein the mass of the plurality of nanostructures comprising the oxide of manganese to the mass of the frustule is about 1:1 to about 100:1.

790. The frustule of embodiment 788, wherein the mass of the plurality of nanostructures comprising the oxide of manganese to the mass of the frustule is about 20:1 to about 100:1.

791. The electrode of any one of embodiments 598 to 603 and 606 to 612, 615 to 619, wherein a mass of the plurality of nanostructures to a mass of at least one frustule of the plurality of frustules is about 1:20 to about 100:1.

792. The electrode of embodiment 791, wherein the mass of the plurality of nanostructures to the mass of the at least one frustule is about 1:1 to about 100:1.

793. The electrode of embodiment 791, wherein the mass of the plurality of nanostructures to the mass of the at least one frustule is about 20:1 to about 100:1.

794. The method of any one of embodiments 620 to 643, wherein a mass of the zinc oxide to a mass of at least one frustule of the plurality of frustules is about 1:20 to about 100:1.

795. The method of embodiment 794, wherein the mass of the zinc oxide to the mass of the at least one frustule is about 1:1 to about 100:1.

796. The method of embodiment 794, wherein the mass of the zinc oxide to the mass of the at least one frustule is about 20:1 to about 100:1.

797. The method of any one of embodiments 645 to 655, wherein a mass of the nanostructures comprising the oxide of manganese to a mass of at least one frustule of the plurality of frustules is about 1:20 to about 100:1.

798. The method of embodiment 797, wherein the mass of the nanostructures comprising the oxide of manganese to the mass of the at least one frustule is about 1:1 to about 100:1.

799. The method of embodiment 797, wherein the mass of the nanostructures comprising the oxide of manganese to the mass of the at least one frustule is about 20:1 to about 100:1.

800. The ink of any one of embodiments 656 to 658, 660 to 667 and 669 to 683, wherein a mass of the plurality of nanostructures to a mass of at least one frustule of the plurality of frustules is about 1:20 to about 100:1.

801. The ink of embodiment 800, wherein the mass of the plurality of nanostructures to the mass of the at least one frustule is about 1:1 to about 100:1.

802. The ink of embodiment 800, wherein a mass of the plurality of nanostructures to the mass of the at least one frustule is about 20:1 to about 100:1.

803. A supercapacitor comprising a pair of electrodes and an electrolyte comprising an ionic liquid, wherein at least one of the electrodes comprises a plurality of frustules having formed thereon a surface active material.

804. The super capacitor of embodiment 803, wherein each of the plurality of frustules is coated with the surface active material.

805. The supercapacitor of embodiments 803 or 804, wherein a first one of the electrodes comprises the frustules.

806. The supercapacitor of any one of embodiments 803 to 805, wherein each of the pair of electrodes comprises the frustules.

807. The supercapacitor of any one of embodiments 803 to 806, wherein no ion transport occurs from one electrode to the other as part of an electrochemical reaction during charge or discharge.

808. The supercapacitor of any one of embodiments 803 to 807, wherein the supercapacitor is configured to be charged to have a voltage difference between the electrodes that exceeds 2 volts.

809. The supercapacitor of any one of embodiments 803 to 808, wherein the ionic liquid comprises a molten salt.

810. The supercapacitor of any one of embodiments 803 to 809, wherein the surface active material comprises nanostructures formed on surfaces of the frustules.

811. The supercapacitor of any one of embodiments 803 to 810, wherein the surface active material comprises nanostructures covering substantially all surfaces of the frustules.

812. The supercapacitor of any one of embodiments 803 to 811, wherein at least one of the electrodes is configured substantially as one or both of an electric double layer capacitor and a pseudo capacitor.

813. The supercapacitor of any one of embodiments 803 to 812, wherein at least one of the electrodes is configured substantially as one of an electric double layer capacitor or a pseudo capacitor while not being configured substantially as the other of the double layer capacitor or the pseudo capacitor.

814. The supercapacitor of any one of embodiments 803 to 813, wherein upon application of a voltage across the electrodes, a first sheet of charge of first polarity forms at surfaces of the surface active material of the at least one of the electrodes configured as an electric double layer capacitor, and a second sheet of charge of second polarity forms adjacent to the at least one of the electrodes configured as the double layer capacitor, wherein the first and second sheets of charge are interposed by a layer of the electrolyte.

815. The supercapacitor of any one of embodiments 803 to 814, wherein upon application of a voltage across the electrodes, the at least one of the electrodes configured as a pseudo capacitor stores energy by a reversible Faradaic redox reaction on the surface of the surface active material.

816. The supercapacitor of any one of embodiments 803 to 815, wherein the surface active material of at least one of the electrodes comprises carbon nanotubes (CNTs).

817. The supercapacitor of embodiment 816, wherein the surface active material of each of the pair of the electrodes comprises the CNTs.

818. The supercapacitor of embodiments 816 or 817, wherein the surface active material comprises the CNTs formed on a surface of each of the frustules.

819. The supercapacitor of any one of embodiments 816 to 818, wherein the at least one of the electrodes comprising the CNTs are configured substantially as an electric double layer capacitor.

820. The supercapacitor of any one of embodiments 803 to 815, wherein the surface active material of at least one of the electrodes comprises one or both of a zinc oxide and a manganese oxide.

821. The supercapacitor of embodiment 820, wherein the surface active material of the at least one of the electrodes comprises one or both of zinc oxide nanoparticles and manganese oxide nanoparticles.

822. The supercapacitor of embodiments 820 or 821, wherein the surface active material of the at least one of the electrodes comprises one or both of the zinc oxide nanoparticles and the manganese oxide nanoparticle formed on a surface of each of the frustules.

823. The supercapacitor of any one of embodiments 820 to 822, wherein the surface active material of each of the pair of the electrodes comprises one or both of the zinc oxide and the manganese oxide.

824. The supercapacitor of any one of embodiments 820 to 823, wherein the at least one of the electrodes comprising one or both of the zinc oxide and the manganese oxide are configured substantially as a pseudo capacitor.

825. The supercapacitor of any one of embodiments 803 to 815, wherein the surface active material of at least one of

the electrodes comprises one but not the other of the zinc oxide and the manganese oxide.

826. The supercapacitor of any one of embodiments 820 to 825, wherein the manganese oxide comprises one or more of manganese dioxide (MnO_2), manganese(II, III) oxide (Mn_3O_4), manganese(II) oxide (MnO), manganese(III) oxide (Mn_2O_3).

827. The supercapacitor of any one of embodiments 816 to 826, wherein the surface active material of one of the pair of electrodes comprises CNTs and the surface active material of the other of pair of electrodes comprises one or both of the zinc oxide and the manganese oxide.

828. The supercapacitor of any one of embodiments 803 to 827, wherein the ionic liquid comprises one or more cations selected from the group consisting of butyltrimethylammonium, 1-ethyl-3-methylimidazolium, 1-butyl-3-methylimidazolium, 1-methyl-3-propylimidazolium, 1-hexyl-3-methylimidazolium, choline, ethylammonium, tributylmethylphosphonium, tributyl(tetradecyl)phosphonium, trihexyl(tetradecyl)phosphonium, 1-ethyl-2,3-methylimidazolium, 1-butyl-1-methylpiperidinium, diethylmethylsulfonium, 1-methyl-3-propylimidazolium, 1-ethyl-3-methylimidazolium, 1-methyl-1-propylpiperidinium, 1-butyl-2-methylpyridinium, 1-butyl-4-methylpyridinium, 1-butyl-1-methylpyrrolidinium, diethylmethylsulfonium and combinations thereof.

829. The supercapacitor of any one of embodiments 803 to 828, wherein the ionic liquid comprises or more anions selected from the group consisting of tris(pentafluoroethyl) trifluorophosphate, trifluoromethanesulfonate, hexafluorophosphate, tetrafluoroborate, ethyl sulfate, dimethyl phosphate, methansulfonate, triflate, tricyanomethanide, dibutylphosphate, bis(trifluoromethylsulfonyl)imide, bis-2,4,4-(trimethylpentyl) phosphinate, iodide, chloride, bromide, nitrate and combinations thereof.

830. The supercapacitor of any one of embodiments 803 to 829, wherein the ionic liquid comprises 1-ethyl-3-methylimidazolium tetrafluoroborate (C_2mimBF_4).

831. The supercapacitor of any one of embodiments 803 to 830, wherein the electrolyte further comprises a salt dissolved therein.

832. The supercapacitor of embodiment 831, wherein the salt has at least a cation that is different from a cation of the ionic liquid.

833. The supercapacitor of embodiments 831 or 832, wherein the salt comprises a cation selected from a group consisting of zinc, sodium, potassium, magnesium, calcium, aluminum, lithium, barium and combinations thereof.

834. The supercapacitor of any one of embodiments 831 to 833, wherein the salt comprises at least an anion that is different from an anion of the ionic liquid.

835. The supercapacitor of any one of embodiments 831 to 834, wherein the salt comprises an anion selected from the group consisting of chloride, bromide, fluoride, bis(trifluoromethanesulfonyl)imide, sulfate, bisulfite, nitrate, nitrite, carbonate, hydroxide, perchloride, bicarbonate, tetrafluoroborate, methansulfonate, acetate, phosphate, citrate, hexafluorophosphate and combinations thereof.

836. The supercapacitor of any one of embodiments 831 to 835, wherein the salt comprises an organic salt.

837. The supercapacitor of any one of embodiments 831 to 836, wherein the salt comprises an anion selected from the group consisting of tetraethylammonium tetrafluoroborate, tetraethylammonium difluoro(oxalate)borate, methylammonium tetrafluoroborate, triethylmethylammonium tetrafluoroborate, tetrafluoroboric acid dimethyldi ethylammonium, triethylmethylammonium tetrafluoroborate, tetrapropylammonium tetrafluoroborate, methyltributylammonium tetrafluoroborate, tetrabutylammonium tetrafluoroborate, tetrahexylammonium tetrafluoroborate, tetramethylammonium tetrafluoroborate, tetraethyl phosphonium tetrafluoroborate, tetrapropylphosphonium tetrafluoroborate, tetrabutylphosphonium, tetrafluoroborate and combinations thereof.

838. The supercapacitor of any one of embodiments 831 to 836, wherein the salt comprises an inorganic salt.

839. The supercapacitor of embodiment 838, wherein the inorganic salt comprises a salt selected from the group consisting of LiCl; Li_2SO_4, $LiClO_4$, NaCl, Na_2SO_4, $NaNO_3$, KCl, K_2SO_4, KNO_3, $Ca(NO_3)_2$, $MgSO_4$ and combinations thereof.

840. The supercapacitor of any one of embodiments 803 to 839, wherein the electrolyte comprises an acid selected from the group consisting of H_2SO_4, HCl, HNO_3, $HClO_4$ and combinations thereof.

841. The supercapacitor of any one of embodiments 803 to 839, wherein the electrolyte comprises a base selected from the group consisting of KOH, NaOH, LiOH, NH_4OH and combinations thereof.

842. The supercapacitor of any one of embodiments 831 to 833 and 835 to 841, wherein the salt comprises the same anion as an anion of the ionic liquid.

843. The supercapacitor of embodiment 838, wherein the salt comprises zinc tetrafluoroborate $Zn(BF_4)_2$.

844. The supercapacitor of any one of embodiments 803 to 843, further comprising a separator interposed between the pair of electrodes.

845. The supercapacitor of embodiment 844, wherein the separator comprises a plurality of frustules.

846. The supercapacitor of embodiment 845, wherein the separator further comprises graphene oxide.

847. The supercapacitor of any one of embodiments 803 to 846, wherein the frustules comprise chemically unmodified frustules.

848. A supercapacitor comprising a pair of electrodes contacting an electrolyte, wherein at least one of the electrodes comprise a plurality of frustules and a zinc oxide.

849. The supercapacitor of embodiment 848, wherein each of the frustules is coated with the zinc oxide.

850. The supercapacitor of embodiments 848 or 849, wherein each of the frustules is coated with nanostructures comprising the zinc oxide.

851. The supercapacitor of any one of embodiments 848 to 850, wherein one or both of the electrodes further comprise carbon nanotubes (CNTs).

852. The supercapacitor of embodiment 848, wherein one of the electrodes comprises the zinc oxide and the other of the electrodes comprises carbon nanotubes (CNTs).

853. The supercapacitor of embodiments 851 or 852, wherein each of the frustules are coated with the CNTs.

854. The supercapacitor of any one of embodiments 848 to 853, wherein the electrolyte comprises an aqueous electrolyte.

855. The supercapacitor of any one of embodiments 848 to 853, wherein the electrolyte comprises a non-aqueous electrolyte.

856. The supercapacitor of any one of embodiments 848 to 855, wherein no ion transport occurs from one electrode to the other as part of an electrochemical reaction during charge or discharge.

857. The supercapacitor of any one of embodiments 848 to 856, wherein at least one of the electrodes is configured substantially as one or both of an electric double layer capacitor and a pseudo capacitor.

858. The supercapacitor of any one of embodiments 848 to 857, wherein at least one of the electrodes is configured substantially as one of an electric double layer capacitor or a pseudo capacitor while not being configured substantially as the other of the double layer capacitor or the pseudo capacitor.

859. The supercapacitor of any one of embodiments 848 to 858, wherein upon application of a voltage across the electrodes, a first sheet of charge of first polarity forms at surfaces of the surface active material of the at least one of the electrodes configured as an electric double layer capacitor, and a second sheet of charge of second polarity forms adjacent to the at least one of the electrodes configured as the double layer capacitor, wherein the first and second sheets of charge are interposed by a layer of electrolyte.

860. The supercapacitor of any one of embodiments 848 to 859, wherein upon application of a voltage across the electrodes, the at least one of the electrodes configured as a pseudo capacitor stores energy by a reversible Faradaic redox reaction on the surface of the surface active material.

861. The supercapacitor of any one of embodiments 848 to 860, wherein the at least one of the electrodes comprising the zinc oxide are configured substantially as a pseudo capacitor.

862. The supercapacitor of any one of embodiments 848 to 861, wherein the at least one of the electrodes comprising the CNTs are configured substantially as an electric double layer capacitor.

863. The supercapacitor of any one of embodiments 848 to 861, wherein the electrolyte comprises an ionic liquid.

864. The supercapacitor of any one of embodiments 848 to 863, wherein the ionic liquid comprises one or more cations selected from the group consisting of butyltrimethylammonium, 1-ethyl-3-methylimidazolium, 1-butyl-3-methylimidazolium, 1-methyl-3-propylimidazolium, 1-hexyl-3-methylimidazolium, choline, ethylammonium, tributylmethylphosphonium, tributyl(tetradecyl)phosphonium, trihexyl(tetradecyl)phosphonium, 1-ethyl-2,3-methylimidazolium, 1-butyl-1-methylpiperidinium, diethylmethylsulfonium, 1-methyl-3-propylimidazolium, 1-ethyl-3-methylimidazolium, 1-methyl-1-propylpiperidinium, 1-butyl-2-methylpyridinium, 1-butyl-4-methylpyridinium, 1-butyl-1-methylpyrrolidinium, diethylmethylsulfonium and combinations thereof.

865. The supercapacitor of any one of embodiments 848 to 864, wherein the ionic liquid comprises or more anions selected from the group consisting of tris(pentafluoroethyl) trifluorophosphate, trifluoromethanesulfonate, hexafluorophosphate, tetrafluoroborate, ethyl sulfate, dimethyl phosphate, methansulfonate, triflate, tricyanomethanide, dibutylphosphate, bis(trifluoromethylsulfonyl)imide, bis-2,4,4-(trimethylpentyl) phosphinate, iodide, chloride, bromide, nitrate and combinations thereof.

866. The supercapacitor of any one of embodiments 848 to 865, wherein the ionic liquid comprises 1-ethyl-3-methylimidazolium tetrafluoroborate (C_2mimBF_4).

867. The supercapacitor of any one of embodiments 848 to 866, wherein the electrolyte further comprises a salt dissolved therein.

868. The supercapacitor of embodiment 867, wherein the salt has at least a cation that is different from a cation of the ionic liquid.

869. The supercapacitor of embodiments 867 or 868, wherein the salt comprises a cation selected from a group consisting of zinc, sodium, potassium, magnesium, calcium, aluminum, lithium, barium and combinations thereof.

870. The supercapacitor of any one of embodiments 867 to 869, wherein the salt comprises at least an anion that is different from an anion of the ionic liquid.

871. The supercapacitor of any one of embodiments 867 to 870, wherein the salt comprises an anion selected from the group consisting of chloride, bromide, fluoride, bis(trifluoromethanesulfonyl)imide, sulfate, bisulfite, nitrate, nitrite, carbonate, hydroxide, perchloride, bicarbonate, tetrafluoroborate, methansulfonate, acetate, phosphate, citrate, hexafluorophosphate and combinations thereof.

872. The supercapacitor of any one of embodiments 867 to 871, wherein the salt comprises an organic salt.

873. The super capacitor of any one of embodiments 867 to 872, wherein the salt comprises an anion selected from the group consisting of tetraethylammonium tetrafluoroborate, tetraethylammonium difluoro(oxalate)borate, methylammonium tetrafluoroborate, triethylmethylammonium tetrafluoroborate, tetrafluoroboric acid dimethyldi ethylammonium, triethylmethylammonium tetrafluoroborate, tetrapropylammonium tetrafluoroborate, methyltributylammonium tetrafluoroborate, tetrabutylammonium tetrafluoroborate, tetrahexylammonium tetrafluoroborate, tetramethylammonium tetrafluoroborate, tetraethyl phosphonium tetrafluoroborate, tetrapropylphosphonium tetrafluoroborate, tetrabutylphosphonium, tetrafluoroborate and combinations thereof.

874. The supercapacitor of any one of embodiments 867 to 871, wherein the salt comprises an inorganic salt.

875. The supercapacitor of embodiment 874, wherein the inorganic salt comprises a salt selected from the group consisting of LiCl; Li_2SO_4, $LiClO_4$, NaCl, Na_2SO_4, $NaNO_3$, KCl, K_2SO_4, KNO_3, $Ca(NO_3)_2$, $MgSO_4$ and combinations thereof.

876. The supercapacitor of any one of embodiments 848 to 874, wherein the electrolyte comprises an acid selected from the group consisting of H_2SO_4, HCl, HNO_3, $HClO_4$ and combinations thereof.

877. The supercapacitor of any one of embodiments 848 to 874, wherein the electrolyte comprises a base selected from the group consisting of KOH, NaOH, LiOH, NH_4OH and combinations thereof.

878. The supercapacitor of any one of embodiments 867 to 869 and 870 to 877, wherein the salt comprises the same anion as an anion of the ionic liquid.

879. The supercapacitor of embodiment 878, wherein the salt comprises zinc tetrafluoroborate $Zn(BF_4)_2$.

880. The supercapacitor of any one of embodiments 848 to 879, further comprising a separator interposed between the pair of electrodes.

881. The supercapacitor of embodiment 880, wherein the separator comprises a plurality of frustules.

882. The supercapacitor of embodiment 881, wherein the separator further comprises graphene oxide.

883. The supercapacitor of any one of embodiments 848 to 882, wherein the frustules comprise chemically unmodified frustules.

884. A supercapacitor comprising a pair of electrodes contacting a non-aqueous electrolyte, wherein at least one of the electrodes comprise a plurality of frustules and a manganese oxide.

885. The supercapacitor of embodiment 884, wherein each of the frustules are coated with the manganese oxide.

886. The supercapacitor of embodiments 884 or 885, wherein each of the frustules are coated with nanostructures comprising the manganese oxide.

887. The supercapacitor of any one of embodiments 884 to 886, wherein the at least one of the electrodes further comprise zinc oxide.

888. The supercapacitor of any one of embodiments 884 to 887, wherein each of the frustules are coated with the zinc oxide.

889. The supercapacitor of any one of embodiments 884 to 888, wherein each of the frustules are coated with nanostructures comprising the zinc oxide.

890. The supercapacitor of any one of embodiments 884 to 889, wherein one or both of the electrodes further comprise carbon nanotubes (CNTs).

891. The supercapacitor of embodiment 884, wherein one of the electrodes comprises the manganese oxide and the other of the electrodes comprises carbon nanotubes (CNTs).

892. The supercapacitor of embodiments 890 or 891, wherein each of the frustules are coated with the CNTs.

893. The supercapacitor of any one of embodiments 884 to 892, wherein the manganese oxide comprises one or more of manganese dioxide (MnO_2), manganese(II, III) oxide (Mn_3O_4), manganese(II) oxide (MnO), manganese(III) oxide (Mn_2O_3).

894. The supercapacitor of any one of embodiments 884 to 893, wherein no ion transport occurs from one electrode to the other as part of an electrochemical reaction during charge or discharge.

895. The supercapacitor of any one of embodiments 884 to 894, wherein at least one of the electrodes is configured substantially as one or both of an electric double layer capacitor and a pseudo capacitor.

896. The supercapacitor of any one of embodiments 884 to 895, wherein at least one of the electrodes is configured substantially as one of an electric double layer capacitor or a pseudo capacitor while not being configured substantially as the other of the double layer capacitor or the pseudo capacitor.

897. The supercapacitor of any one of embodiments 884 to 896, wherein upon application of a voltage across the electrodes, a first sheet of charge of first polarity forms at surfaces of the surface active material of the at least one of the electrodes configured as an electric double layer capacitor, and a second sheet of charge of second polarity forms adjacent to the at least one of the electrodes configured as the double layer capacitor, wherein the first and second sheets of charge are interposed by a layer of electrolyte.

898. The supercapacitor of any one of embodiments 884 to 897, wherein upon application of a voltage across the electrodes, the at least one of the electrodes configured as a pseudo capacitor stores energy by a reversible Faradaic redox reaction on the surface of the surface active material.

899. The supercapacitor of any one of embodiments 884 to 899, wherein the at least one of the electrodes comprising the zinc oxide are configured substantially as a pseudo capacitor.

900. The supercapacitor of any one of embodiments 890 to 892, wherein the at least one of the electrodes comprising the CNTs are configured substantially as an electric double layer capacitor.

901. The supercapacitor of any one of embodiments 884 to 900, wherein the electrolyte comprises an ionic liquid.

902. The supercapacitor of any one of embodiments 884 to 901, wherein the ionic liquid comprises one or more cations selected from the group consisting of butyltrimethylammonium, 1-ethyl-3-methylimidazolium, 1-butyl-3-methylimidazolium, 1-methyl-3-propylimidazolium, 1-hexyl-3-methylimidazolium, choline, ethylammonium, tributylmethylphosphonium, tributyl(tetradecyl)phosphonium, trihexyl(tetradecyl)phosphonium, 1-ethyl-2,3-methylimidazolium, 1-butyl-1-methylpiperidinium, diethylmethylsulfonium, 1-methyl-3-propylimidazolium, 1-ethyl-3-methylimidazolium, 1-methyl-1-propylpiperidinium, 1-butyl-2-methylpyridinium, 1-butyl-4-methylpyridinium, 1-butyl-1-methylpyrrolidinium, diethylmethylsulfonium and combinations thereof.

903. The supercapacitor of any one of embodiments 884 to 902, wherein the ionic liquid comprises or more anions selected from the group consisting of tris(pentafluoroethyl) trifluorophosphate, trifluoromethanesulfonate, hexafluorophosphate, tetrafluoroborate, ethyl sulfate, dimethyl phosphate, methansulfonate, triflate, tricyanomethanide, dibutylphosphate, bis(trifluoromethylsulfonyl)imide, bis-2,4,4-(trimethylpentyl) phosphinate, iodide, chloride, bromide, nitrate and combinations thereof.

904. The supercapacitor of any one of embodiments 884 to 903, wherein the ionic liquid comprises 1-ethyl-3-methylimidazolium tetrafluoroborate (C_2mimBF_4).

905. The supercapacitor of any one of embodiments 884 to 904, wherein the electrolyte further comprises a salt dissolved therein.

906. The supercapacitor of embodiment 905, wherein the salt has at least a cation that is different from a cation of the ionic liquid.

907. The supercapacitor of embodiments 905 or 906, wherein the salt comprises a cation selected from a group consisting of zinc, sodium, potassium, magnesium, calcium, aluminum, lithium, barium and combinations thereof.

908. The supercapacitor of any one of embodiments 905 to 907, wherein the salt comprises at least an anion that is different from an anion of the ionic liquid.

909. The supercapacitor of any one of embodiments 905 to 908, wherein the salt comprises an anion selected from the group consisting of chloride, bromide, fluoride, bis(trifluoromethanesulfonyl)imide, sulfate, bisulfite, nitrate, nitrite, carbonate, hydroxide, perchloride, bicarbonate, tetrafluoroborate, methansulfonate, acetate, phosphate, citrate, hexafluorophosphate and combinations thereof.

910. The supercapacitor of any one of embodiments 905 to 909, wherein the salt comprises an organic salt.

911. The super capacitor of any one of embodiments 905 to 910, wherein the salt comprises an anion selected from the group consisting of tetraethylammonium tetrafluoroborate, tetraethylammonium difluoro(oxalate)borate, methylammonium tetrafluoroborate, triethylmethylammonium tetrafluoroborate, tetrafluoroboric acid dimethyldi ethylammonium, triethylmethylammonium tetrafluoroborate, tetrapropylammonium tetrafluoroborate, methyltributylammonium tetrafluoroborate, tetrabutylammonium tetrafluoroborate, tetrahexylammonium tetrafluoroborate, tetramethylammonium tetrafluoroborate, tetraethyl phosphonium tetrafluoroborate, tetrapropylphosphonium tetrafluoroborate, tetrabutylphosphonium, tetrafluoroborate and combinations thereof.

912. The supercapacitor of any one of embodiments 905 to 909, wherein the salt comprises an inorganic salt.

913. The supercapacitor of embodiment 912, wherein the inorganic salt comprises a salt selected from the group consisting of LiCl; Li_2SO_4, $LiClO_4$, NaCl, Na_2SO_4, $NaNO_3$, KCl, K_2SO_4, KNO_3, $Ca(NO_3)_2$, $MgSO_4$ and combinations thereof.

914. The supercapacitor of any one of embodiments 884 to 913, wherein the electrolyte comprises an acid selected from the group consisting of H_2SO_4, HCl, HNO_3, $HClO_4$ and combinations thereof.

915. The supercapacitor of any one of embodiments 884 to 913, wherein the electrolyte comprises a base selected from the group consisting of KOH, NaOH, LiOH, NH_4OH and combinations thereof.

916. The supercapacitor of any one of embodiments 905 to 907 and 909 to 915, wherein the salt comprises the same anion as an anion of the ionic liquid.

917. The supercapacitor of embodiment 905, wherein the salt comprises zinc tetrafluoroborate $Zn(BF_4)_2$.

918. The supercapacitor of any one of embodiments 905 to 917, further comprising a separator interposed between the pair of electrodes.

919. The supercapacitor of embodiment 918, wherein the separator comprises a plurality of frustules.

920. The supercapacitor of embodiment 919, wherein the separator further comprises graphene oxide.

921. The supercapacitor of any one of embodiments 905 to 921, wherein the frustules comprise chemically unmodified frustules.

922. A supercapacitor comprising a pair of electrodes contacting an electrolyte, wherein at least one of the electrodes comprise a plurality of frustules and carbon nanotubes (CNTs).

923. The supercapacitor of embodiment 922, wherein a surface of each of the frustules has one or more of the CNTs formed thereon.

924. The supercapacitor of embodiments 922 or 923, wherein at least one of the electrodes further comprise at least one of zinc oxide and manganese oxide.

925. The supercapacitor of any one of embodiments 922 to 924, wherein the surface of each of the frustules has one or more of the at least one of the zinc oxide and the manganese oxide formed thereon.

926. The supercapacitor of any one of embodiments 922 to 925, wherein the surface of each of the frustules has formed thereon nanostructures comprising the at least one of the zinc oxide and the manganese oxide.

927. The supercapacitor of any one of embodiments 924 to 926, wherein the manganese oxide comprises one or more of manganese dioxide (MnO_2), manganese(II, III) oxide (Mn_3O_4), manganese(II) oxide (MnO), manganese(III) oxide (Mn_2O_3).

928. The supercapacitor of any one of embodiments 922 to 927, wherein no ion transport occurs from one electrode to the other as part of an electrochemical reaction during charge or discharge.

929. The supercapacitor of any one of embodiments 922 to 928, wherein at least one of the electrodes is configured substantially as one or both of an electric double layer capacitor and a pseudo capacitor.

930. The supercapacitor of any one of embodiments 922 to 929, wherein at least one of the electrodes is configured substantially as one of an electric double layer capacitor or a pseudo capacitor while not being configured substantially as the other of the double layer capacitor or the pseudo capacitor.

931. The supercapacitor of any one of embodiments 922 to 930, wherein upon application of a voltage across the electrodes, a first sheet of charge of first polarity forms at surfaces of the surface active material of the at least one of the electrodes configured as an electric double layer capacitor, and a second sheet of charge of second polarity forms adjacent to the at least one of the electrodes configured as the double layer capacitor, wherein the first and second sheets of charge are interposed by a layer of electrolyte.

932. The supercapacitor of any one of embodiments 922 to 931, wherein upon application of a voltage across the electrodes, the at least one of the electrodes configured as a pseudo capacitor stores energy by a reversible Faradaic redox reaction on the surface of the surface active material.

933. The supercapacitor of any one of embodiments 922 to 932, wherein the at least one of the electrodes comprising the at least one of the zinc oxide and the manganese oxide are configured substantially as a pseudo capacitor.

934. The supercapacitor of any one of embodiments 922 to 932, wherein the at least one of the electrodes are configured substantially as an electric double layer capacitor.

935. The supercapacitor of any one of embodiments 922 to 934, wherein the electrolyte comprises an ionic liquid.

936. The supercapacitor of any one of embodiments 922 to 935, wherein the ionic liquid comprises one or more cations selected from the group consisting of butyltrimethylammonium, 1-ethyl-3-methylimidazolium, 1-butyl-3-methylimidazolium, 1-methyl-3-propylimidazolium, 1-hexyl-3-methylimidazolium, choline, ethylammonium, tributylmethylphosphonium, tributyl(tetradecyl)phosphonium, trihexyl(tetradecyl)phosphonium, 1-ethyl-2,3-methylimidazolium, 1-butyl-1-methylpiperidinium, diethylmethylsulfonium, 1-methyl-3-propylimidazolium, 1-ethyl-3-methylimidazolium, 1-methyl-1-propylpiperidinium, 1-butyl-2-methylpyridinium, 1-butyl-4-methylpyridinium, 1-butyl-1-methylpyrrolidinium, diethylmethylsulfonium and combinations thereof.

937. The supercapacitor of any one of embodiments 922 to 936, wherein the ionic liquid comprises or more anions selected from the group consisting of tris(pentafluoroethyl) trifluorophosphate, trifluoromethanesulfonate, hexafluorophosphate, tetrafluoroborate, ethyl sulfate, dimethyl phosphate, methansulfonate, triflate, tricyanomethanide, dibutylphosphate, bis(trifluoromethylsulfonyl)imide, bis-2,4,4-(trimethylpentyl) phosphinate, iodide, chloride, bromide, nitrate and combinations thereof.

938. The supercapacitor of embodiment 935, wherein the ionic liquid comprises 1-ethyl-3-methylimidazolium tetrafluoroborate (C_2mimBF_4).

939. The supercapacitor of any one of embodiments 922 to 938, wherein the electrolyte further comprises a salt dissolved therein.

940. The supercapacitor of embodiment 939, wherein the salt has at least a cation that is different from a cation of the ionic liquid.

941. The supercapacitor of embodiments 939 or 940, wherein the salt comprises a cation selected from a group consisting of zinc, sodium, potassium, magnesium, calcium, aluminum, lithium, barium and combinations thereof.

942. The supercapacitor of any one of embodiments 939 to 941, wherein the salt comprises at least an anion that is different from an anion of the ionic liquid.

943. The supercapacitor of any one of embodiments 939 to 942, wherein the salt comprises an anion selected from the group consisting of chloride, bromide, fluoride, bis(trifluoromethanesulfonyl)imide, sulfate, bisulfite, nitrate, nitrite, carbonate, hydroxide, perchloride, bicarbonate, tetrafluoroborate, methansulfonate, acetate, phosphate, citrate, hexafluorophosphate and combinations thereof.

944. The supercapacitor of any one of embodiments 939 to 943, wherein the salt comprises an organic salt.

945. The supercapacitor of any one of embodiments 939 to 944, wherein the salt comprises an anion selected from the group consisting of tetraethylammonium tetrafluoroborate, tetraethylammonium difluoro(oxalate)borate, methylammonium tetrafluoroborate, triethylmethylammonium tetrafluoroborate, tetrafluoroboric acid dimethyldi ethylammonium, triethylmethylammonium tetrafluoroborate, tetrapropylammonium tetrafluoroborate, methyltributylammonium tetrafluoroborate, tetrabutylammonium tetrafluoroborate, tetra-

hexylammonium tetrafluoroborate, tetramethylammonium tetrafluoroborate, tetraethyl phosphonium tetrafluoroborate, tetrapropylphosphonium tetrafluoroborate, tetrabutylphosphonium, tetrafluoroborate and combinations thereof.

946. The supercapacitor of any one of embodiments 939 to 943, wherein the salt comprises an inorganic salt.

947. The supercapacitor of embodiment 946, wherein the inorganic salt comprises a salt selected from the group consisting of LiCl; Li_2SO_4, $LiClO_4$, NaCl, Na_2SO_4, $NaNO_3$, KCl, K_2SO_4, KNO_3, $Ca(NO_3)_2$, $MgSO_4$ and combinations thereof.

948. The supercapacitor of any one of embodiments 922 to 947, wherein the electrolyte comprises an acid selected from the group consisting of H_2SO_4, HCl, HNO_3, $HClO_4$ and combinations thereof.

949. The supercapacitor of any one of embodiments 922 to 947, wherein the electrolyte comprises a base selected from the group consisting of KOH, NaOH, LiOH, NH_4OH and combinations thereof.

950. The supercapacitor of any one of embodiments 939 to 941 and 943 to 949, wherein the salt comprises the same anion as an anion of the ionic liquid.

951. The supercapacitor of embodiment 950, wherein the salt comprises zinc tetrafluoroborate $Zn(BF_4)_2$.

952. The supercapacitor of any one of embodiments 922 to 951, further comprising a separator interposed between the pair of electrodes.

953. The supercapacitor of embodiment 952, wherein the separator comprises a plurality of frustules.

954. The supercapacitor of embodiment 953, wherein the separator further comprises graphene oxide.

955. The supercapacitor of any one of embodiments 922 to 954, wherein the frustules comprise chemically unmodified frustules.

956. A method of fabricating a supercapacitor, the method comprising: forming a separator between a pair of electrodes, wherein the separator comprises frustules, an electrolyte and a thermally conductive additive, wherein the thermally conductive additive is adapted to substantially absorb a near infrared (NIR) radiation upon being applied to the separator, thereby causing heating of the separator to accelerate drying.

957. The method of embodiment 956, wherein the thermally conductive additive is substantially thermally conducting and substantially electrically insulating.

958. The method of embodiments 956 or 957, wherein the thermally conductive additive comprises graphene oxide (GO).

959. The method of embodiment 958, wherein the GO comprises a network of contiguous sheets contacting each other.

960. The method of any one of embodiments 956 to 959, wherein the forming the separator comprises forming a mixture comprising the frustules, a gel and the electrolyte.

961. The method of embodiment 960, wherein the electrolyte comprises one or more of a solvent, a salt and an ionic liquid.

962. The method of embodiments 960 or 961, wherein the gel comprises a gelling polymer.

963. The method of embodiment 962, wherein the gelling polymer includes one or more selected from the group consisting of polyvinylidene fluoride, polyacrylic acid, polyethylene oxide, polyvinyl alcohol and combinations thereof.

964. The method of embodiments 962 or 963, wherein the gel comprises the gelling polymer and the electrolyte.

965. The method of any one of embodiments 960 to 964, wherein the frustules form a network of pores, wherein forming the mixture comprises substantially completely filling the network of pores with the gel.

966. The method of any one of embodiments 960 to 964, wherein the frustules form a network of pores, wherein forming the mixture comprises partly filling the network of pores with the gel.

967. The method of embodiment 964, wherein forming the mixture comprises filing the network unfilled with the gel with the electrolyte.

968. The method of any one of embodiments 956-967, wherein forming the separator comprises printing using an ink comprising the frustules and the thermally conductive additive.

969. The method of any one of embodiments 956 to 968, wherein the separator comprises an electrolyte comprising an ionic liquid.

970. The method of embodiment 969, wherein the ionic liquid comprises one or more cations selected from the group consisting of butyltrimethylammonium, 1-ethyl-3-methylimidazolium, 1-butyl-3-methylimidazolium, 1-methyl-3-propylimidazolium, 1-hexyl-3-methylimidazolium, choline, ethylammonium, tributylmethylphosphonium, tributyl(tetradecyl)phosphonium, trihexyl(tetradecyl) phosphonium, 1-ethyl-2,3-methylimidazolium, 1-butyl-1-methylpiperidinium, diethylmethylsulfonium, 1-methyl-3-propylimidazolium, 1-ethyl-3-methylimidazolium, 1-methyl-1-propylpiperidinium, 1-butyl-2-methylpyridinium, 1-butyl-4-methylpyridinium, 1-butyl-1-methylpyrrolidinium, diethylmethylsulfonium and combinations thereof.

971. The method of embodiments 969 or 970, wherein the ionic liquid comprises or more anions selected from the group consisting of tris(pentafluoroethyl)trifluorophosphate, trifluoromethanesulfonate, hexafluorophosphate, tetrafluoroborate, ethyl sulfate, dimethyl phosphate, methansulfonate, triflate, tricyanomethanide, dibutylphosphate, bis(trifluoromethylsulfonyl)imide, bis-2,4,4-(trimethylpentyl) phosphinate, iodide, chloride, bromide, nitrate and combinations thereof.

972. The method of any one of embodiments 969 to 971, wherein the ionic liquid comprises 1-ethyl-3-methylimidazolium tetrafluoroborate (C_2mimBF_4).

973. The method of any one of embodiments 969 to 972, wherein the electrolyte further comprises a salt dissolved therein.

974. The method of embodiment 973, wherein the salt comprises a cation selected from a group consisting of zinc, sodium, potassium, magnesium, calcium, aluminum, lithium, barium and combinations thereof.

975. The method of embodiments 973 or 974, wherein the salt comprises at least an anion that is different from an anion of the ionic liquid.

976. The method of any one of embodiments 973 to 975, wherein the salt comprises an anion selected from the group consisting of chloride, bromide, fluoride, bis(trifluoromethanesulfonyl)imide, sulfate, bisulfite, nitrate, nitrite, carbonate, hydroxide, perchloride, bicarbonate, tetrafluoroborate, methansulfonate, acetate, phosphate, citrate, hexafluorophosphate and combinations thereof.

977. The method of any one of embodiments 973 to 976, wherein the salt comprises an organic salt.

978. The method of any one of embodiments 973 to 977, wherein the salt comprises an anion selected from the group consisting of tetraethylammonium tetrafluoroborate, tetraethylammonium difluoro(oxalate)borate, methylammonium tetrafluoroborate, triethylmethylammonium tetrafluoroborate, tetrafluoroboric acid dimethyldi ethylammonium, tri-

ethylmethylammonium tetrafluoroborate, tetrapropylammonium tetrafluoroborate, methyltributylammonium tetrafluoroborate, tetrabutylammonium tetrafluoroborate, tetrahexylammonium tetrafluoroborate, tetramethylammonium tetrafluoroborate, tetraethyl phosphonium tetrafluoroborate, tetrapropylphosphonium tetrafluoroborate, tetrabutylphosphonium, tetrafluoroborate and combinations thereof.

979. The method of any one of embodiments 973 to 978, wherein the salt comprises an inorganic salt.

980. The method of embodiment 979, wherein the inorganic salt comprises a salt selected from the group consisting of LiCl, Li_2SO_4, $LiClO_4$, NaCl, Na_2SO_4, $NaNO_3$, KCl, K_2SO_4, KNO_3, $Ca(NO_3)_2$, $MgSO_4$ and combinations thereof.

981. The method of any one of embodiments 969 to 980, wherein the electrolyte comprises an acid selected from the group consisting of H_2SO_4, HCl, HNO_3, $HClO_4$ and combinations thereof.

982. The method of any one of embodiments 969 to 980, wherein the electrolyte comprises a base selected from the group consisting of KOH, NaOH, LiOH, NH_4OH and combinations thereof.

983. The method of any one of embodiments 973 to 980, wherein the salt comprises the same anion as an anion of the ionic liquid.

984. The method of any one of embodiments 973 to 980, wherein the salt comprises zinc tetrafluoroborate $Zn(BF_4)_2$.

985. The method of any one of embodiments 956 to 984, further comprising drying the separator by subjecting the separator to the NIR radiation.

986. The method of embodiment 985, wherein drying the separator is performed for a duration not exceeding 1 minute. The method of any one of embodiments 956 to 985, wherein the supercapacitor is according to any one of embodiments 803 to 847.

987. The method of any one of embodiments 956 to 985, wherein the supercacitor is according to any one of embodiments 848 to 883.

988. The method of any one of embodiments 956 to 985, wherein the supercacitor is according to any one of embodiments 884 to 955.

989. The method of any one of embodiments 956 to 985, wherein one or more components of the supercapacitor are manufactured according to the method of manufacturing the printed energy storage device according to any one of embodiments 98 to 115.

990. The method of any one of embodiments 956 to 985, wherein one or more components of the supercapacitor are printed using the ink according to any one of embodiments 116 to 154.

991. The method of any one of embodiments 956 to 985, wherein the frustules are extracted according to any one of embodiments 160 to 321.

992. The method of any one of embodiments 956 to 985, wherein one or more components of the supercapacitor are printed using the ink according to any one of embodiments 520 to 524.

993. The method of any one of embodiments 956 to 985, wherein at least some of the frustules comprise a surface active material comprising manganese-containing nanostructures formed according to any one of embodiments 525 to 546.

994. The method of any one of embodiments 956 to 985, wherein at least some of the frustules comprise a surface active material comprising zinc-oxide nanostructures formed according to any one of embodiments 620 to 644.

995. The method of any one of embodiments 956 to 985, wherein at least some of the frustules comprise a surface active material comprising the oxide of manganese formed according to any one of embodiments 645 to 655.

996. The method of any one of embodiments 956 to 985, wherein one or more components of the supercapacitor are printed using the ink according to any one of embodiments 656 to 683.

997. The method of any one of embodiments 956 to 985, wherein one or more components of the supercapacitor are printed using the ink prepared according to any one of embodiments 684 to 705.

998. The method of any one of embodiments 956 to 985, wherein one or more components of the supercapacitor are formed according to any one of embodiments 706 to 739.

While the methods and devices described herein may be susceptible to various modifications and alternative forms, specific examples thereof have been shown in the drawings and are herein described in detail. It should be understood, however, that the invention is not to be limited to the particular forms or methods disclosed, but, to the contrary, the invention is to cover all modifications, equivalents, and alternatives falling within the spirit and scope of the various implementations described and the appended claims. It is also contemplated that various combinations or sub-combinations of the specific features and aspects of the embodiments may be made and still fall within the scope of the invention. It should be understood that various features and aspects of the disclosed embodiments can be combined with, or substituted for, one another in order to form varying modes of the embodiments of the disclosed invention. Further, the disclosure herein of any particular feature, aspect, method, property, characteristic, quality, attribute, element, or the like in connection with an implementation or embodiment can be used in all other implementations or embodiments set forth herein.

Any methods disclosed herein need not be performed in the order recited. The methods disclosed herein may include certain actions taken by a practitioner; however, the methods can also include any third-party instruction of those actions, either expressly or by implication. For example, actions such as "adding the frustules to an oxygenated manganese acetate solution" include "instructing the adding of the frustules to an oxygenated manganese acetate solution."

The ranges disclosed herein also encompass any and all overlap, sub-ranges, and combinations thereof. Language such as "up to," "at least," "greater than," "less than," "between," and the like includes the number recited. Numbers preceded by a term such as "about" or "approximately" include the recited numbers and should be interpreted based on the circumstances (e.g., as accurate as reasonably possible under the circumstances, for example ±5%, ±10%, ±15%, etc.). For example, "about 3.5 mm" includes "3.5 mm." Phrases preceded by a term such as "substantially" include the recited phrase and should be interpreted based on the circumstances (e.g., as much as reasonably possible under the circumstances). For example, "substantially constant" includes "constant."

The headings provided herein, if any, are for convenience only and do not necessarily affect the scope or meaning of the devices and methods disclosed herein.

What is claimed is:

1. A supercapacitor comprising:

a pair of electrodes contacting an electrolyte,

wherein each of the electrodes comprises a plurality of frustules having formed thereon a manganese oxide, and

wherein the supercapacitor is configured to charge and discharge through an electrochemical process.

2. The supercapacitor of claim **1**, wherein the frustules of one or both of the electrodes further have formed thereon a zinc oxide.

3. The supercapacitor of claim **1**, wherein the frustules of one or both of the electrodes have formed thereon nanostructures comprising the manganese oxide.

4. The supercapacitor of claim **1**, wherein the manganese oxide comprises one or more of manganese dioxide (MnO_2), manganese (II, III) oxide (Mn_3O_4), manganese(II) oxide (MnO), or manganese (III) oxide (Mn_2O_3).

5. The supercapacitor of claim **1**, wherein each of the electrodes is configured as a pseudo capacitor.

6. The supercapacitor of claim **1**, wherein no ion transport occurs between the one of the electrodes and the other of the electrodes as part of an electrochemical reaction during charge or discharge.

7. The supercapacitor of claim **1**, wherein the electrolyte comprises an ionic liquid.

8. The supercapacitor of claim **7**, wherein the ionic liquid comprises one or more cations selected from the group consisting of butyltrimethylammonium, 1-ethyl-3-methylimidazolium, 1-butyl-3-methylimidazolium, 1-methyl-3-propylimidazolium, 1-hexyl-3-methylimidazolium, choline, ethylammonium, tributylmethylphosphonium, tributyl(tetradecyl)phosphonium, trihexyl(tetradecyl)phosphonium, 1-ethyl-2,3-methylimidazolium, 1-butyl-1-methylpiperidinium, diethylmethylsulfonium, 1-methyl-3-propylimidazolium, 1-ethyl-3-methylimidazolium, 1-methyl-1-propylpiperidinium, 1-butyl-2-methylpyridinium, 1-butyl-4-methylpyridinium, 1-butyl-1-methylpyrrolidinium, diethylmethylsulfonium or a combination thereof.

9. The supercapacitor of claim **7**, wherein the ionic liquid comprises or more anions selected from the group consisting of tris(pentafluoroethyl)trifluorophosphate, trifluoromethanesulfonate, hexafluorophosphate, tetrafluoroborate, ethyl sulfate, dimethyl phosphate, methanesulfonate, triflate, tricyanomethanide, dibutylphosphate, bis(trifluoromethylsulfonyl)imide, bis-2,4,4-(trimethylpentyl) phosphinate, iodide, chloride, bromide, nitrate or a combination thereof.

10. A supercapacitor comprising:

a pair of electrodes contacting an electrolyte,

wherein each of the electrodes comprises a plurality of frustules having formed thereon a zinc oxide, and

wherein the supercapacitor is configured to charge and discharge through an electrochemical process.

11. The supercapacitor of claim **10**, wherein the frustules of one or both of the electrodes further have formed thereon a manganese oxide.

12. The supercapacitor of claim **10**, wherein the frustules of one or both of the electrodes have formed thereon nanostructures comprising the zinc oxide.

13. The supercapacitor of claim **11**, wherein the manganese oxide comprises one or more of manganese dioxide (MnO_2), manganese (II, III) oxide (Mn_3O_4), manganese (II) oxide (MnO), or manganese(III) oxide (Mn_2O_3).

14. The supercapacitor of claim **10**, wherein each of the electrodes is configured as a pseudo capacitor.

15. The supercapacitor of claim **10**, wherein no ion transport occurs between the one of the electrodes and the other of the electrodes as part of an electrochemical reaction during charge or discharge.

16. A supercapacitor comprising:

a first electrode comprising a plurality of frustules having formed thereon one or both a manganese oxide and a zinc oxide; and

a second electrode comprising carbon nanotubes,

wherein the supercapacitor is configured to charge and discharge through an electrochemical process.

17. The supercapacitor of claim **16**, wherein the first electrode is configured as a pseudocapacitor and the second electrode is configured as an electric double-layer capacitor.

18. The supercapacitor of claim **16**, wherein the first electrode and the second electrode contact a non-aqueous electrolyte.

19. The supercapacitor of claim **16**, wherein the manganese oxide comprises one or more of manganese dioxide (MnO_2), manganese (II, III) oxide (Mn_3O_4), manganese(II) oxide (MnO), or manganese (III) oxide (Mn_2O_3).

20. The supercapacitor of claim **16**, wherein no ion transport occurs between the one of the electrodes and the other of the electrodes as part of an electrochemical reaction during charge or discharge.

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